JOURNAL OF THE AMERICAN CERAMIC SOCIETY

A · MONTHLY · JOURNAL · DEVOTED · TO · THE · ARTS · AND · SCIENCES
RELATED · TO · THE · SILICATE · INDUSTRIES

ABSTRACTS
VOL. 12 No. 9

VOLUME 16 SEPTEMBER • 1933 NUMBER 9

Table of Contents

SEPTEMBER, 1933

The Journal

Water Movement in Stiff-Mud and Its Relation to Drying—Lovejoy 405

Papers from the Second Symposium on the Physical Chemistry of the Alumina-Silica Refractories—Arranged by Sosman

I. The Rôle of Silicon and Aluminum in Complex Silicates —Warren 412

II. Structure of Sillimanite and Related Materials—Taylor 418

III. Bauxites and Mullites—Nahmias 420

Discussion of the Physical Chemistry of the Alumina-Silica Refractories—Wyckoff 422

Discussion on "Theory of Spalling"—Norton 423

Gases in Glass—Dalton 425

A Peculiarity of Sheet-Iron Acid Resisting Cover Coat Enamels—Ebright and Hansen 433

Progress Report of the Study of Gases in Enameling Iron—Baker and Joublanc 437

A Summary of the Observations and Facts Concerning the Phenomenon of Reboiling—Lord 442

Effect of Organic Grinding Media on Water-Soluble Silicate Frits—Barlett and Schwartzwalder 452

Ceramic Abstracts 319

Publication Office: 20th & Northampton Sts., Easton, Pa.
Editorial and Advertising Offices: 2525 N. High St., Columbus, Ohio.
Executive Office: 2525 N. High St., Columbus, Ohio.
Committee on Publications: L. Navias, *Chairman;* L. J. Trostel, M. F. Beecher, R. M. King, Ross C. Purdy.
Entered as second-class matter at the post office at Easton, Pa., under the Act of March 3, 1879.

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Subscription Twelve dollars a year. Single numbers one dollar
(Foreign and Canadian postage, 50c additional on subscriptions)

IMPORTANT ANNOUNCEMENT

The *Journal of the American Ceramic Society* and *Ceramic Abstracts* for October will be devoted exclusively to "A Compilation of Phase-Rule Diagrams of Interest to the Ceramist and Silicate Technologist."

This compilation will include 175 equilibrium diagrams together with complete literature references.

The work has been compiled by Dr. Flemmon P. Hall and Dr. Herbert Insley.

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The abstracts prepared for October will appear in November in an October-November combination issue.

THE AMERICAN CERAMIC SOCIETY

WATER MOVEMENT IN STIFF-MUD WARE AND ITS RELATION TO DRYING*

By Ellis Lovejoy

ABSTRACT

Stiff-mud test bars were dried from one surface, and the rate of water loss was determined by frequent weighings. The plotted curves indicate an end point in the water movement with a loss of around 60% of the total water. This loss was checked by soluble salts in the clay and alkalinity tests at intervals.

I. Introduction

At a meeting of the National Brick Manufacturers Association in 1929, it was stated that in drying ware there is practically no water movement from inside the ware to the surface and that drying takes place by evaporation from inside the ware. This statement was controverted by the fact that soluble salts (efflorescence) are brought to the surface during the drying period. It was this theory on which information was sought in the investigation herein reported.

II. The Investigation

(1) Procedure Clays were pugged to a stiff-mud consistency and made into one-inch square bars four inches long. Tests were made of clays as received, grogged, treated with electrolytes, and de-aired. The bars were wrapped in tin foil except for the one end to be exposed to the drying. They were dried in an electric drier at a constant temperature of 75°C for 72 hours following which the temperature was advanced to 110° until the bars were fully dry. The drier was a recirculating type and in all of the tests no change was made in the air inlets and exhausts. Other than this no effort was made to control humidity conditions in the drier. Besides the alkalinity tests mentioned in the abstract, a number of tests was correlated with kerosene capillarity of the dry bars as an approximate reversal of the flow of shrinkage water in the drying.

(2) Clays Used and Their Characteristics Data are given on the following clays which were used:

Clays	Water of plasticity (%)	General drying behavior
Ky. ball clay	40.8	Fair
Miss. fire clay	34.7	Good
Groveport, Ohio, surface clay		
(Pugged soft)	28.9	Bad
(Normal pug)	26.6	Bad
Mich. surface clay (not limey)	25.6	Very bad
Texas surface clay (limey)	24.8	Very bad
Bedford shale	22.0	Good
Tionesta fire clay		
(Pugged soft)	24.5	Good
(Normal pug)	19.6	Good
Pa. fire clay (very sandy)	18.7	Good

(3) Results of Tests All of the curves obtained in the tests are uniformly like those shown in Figs. 1 and 2. In all of the tests the lines are straight up to an average of over 60% water loss. This

* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Structural Clay Products Division).

is the shrinkage water loss which would be constant in its rate since it is moved to the drying surface and evaporated from the surface. Evidence of this movement is present in the alkalinity tests. Without such evidence, however, it seems clear that the constant rate (the straight line) is proof of surface supply and evaporation. If this water loss were due to evaporation below the surface the line would be curved as it is for the final evaporation of the pore water.

Norton and Hodgdon[1] showed that the shrinkage of English ball clay and bentonite does not cease with the elimination of shrinkage water (saturation point to critical point); instead, it continues below the critical point to zero water content. Such clays should show curved lines from the start. The shrinkage water in these clays moves with such difficulty that capillary movement can not keep pace with surface evaporation, and the drying would proceed by evaporation within the ware, the adsorbed water loss following that of the shrinkage water as above indicated but closely correlated.

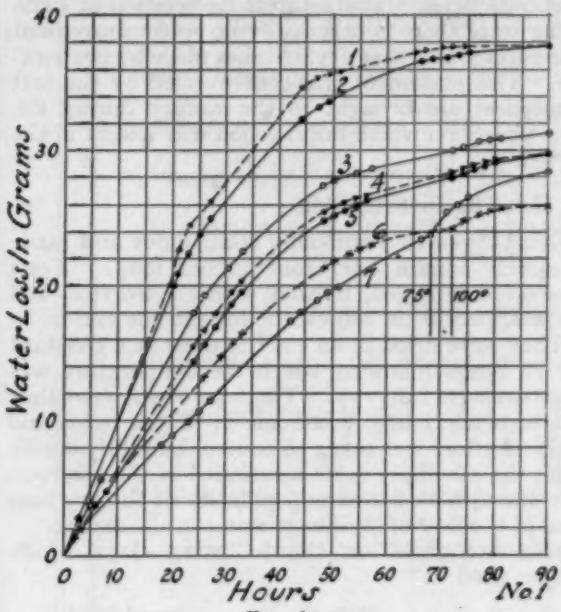

FIG. 1.

There were three curves like that of curve 1 (Fig. 1) in which the line was straight up to a certain point where the line broke, followed by a second straight line, and then the final break in the curve. It is assumed that these broken curves are evidence of an overlapping of the shrinkage water loss and that of the pore water. Undoubtedly there is such overlapping. In curve 7 (Fig. 1), which will be described later, the actual curvature toward the end (below 75°) is slight. In the final drying where the temperature was advanced to 110° there is a big jump in this curve showing that the water was not diminishing as it did in the other cases.

Curve 5 (Fig. 1) is the Texas clay. It has the slowest rate of shrinkage water movement of any of the clays tested. It crosses the 18-gram loss line at 30 hours whereas curve 2 crosses this line at 18 hours, a lag of twelve hours in the rate of shrinkage water movement in curve 5.

(4) Effect of De-Airing

Curve 4 is the Texas de-aired clay test. It closely follows the Texas air-bar test. De-airing will bring laminae in contact, but it has made little difference in the rate of

[1] F. H. Norton and F. B. Hodgdon, *Jour. Amer. Ceram. Soc.*, **15** [3], 191–205 (1932)

shrinkage water flow. The de-aired bar tests, as in the instance shown, were sometimes above the normal clay-bar test and sometimes below, yet with the exception of one test the de-aired curves were close to the normal test curve. In tests of ten clays the de-aired test was above the curve seven times, once widely above, and three times below.

This gives de-airing a slight advantage in rate of water flow. It is surmised that were the water moving across the laminae instead of with them there would be a wide difference in favor of rapid flow in the de-aired tests. The effect of structure is a big factor. Curve 7 shows the results for hand-molded Texas clay. The rate of water movement is much slower than in the machine bar from the same clay (curve 5).

(5) Effect of Grog Curve 6 is the Texas clay containing 20% grog. In every test with grog except one there was a slower water movement than in the clay alone.

The grogged test lagged the clay test by seven hours on the 18-gram line. This was unexpected since the writer had a preconceived idea that grog opened the pores of the mass and thus permitted the water to flow more freely. There is no reason, however, why grog should thus provide pore spaces. The water still would have to flow through the plastic matrix and would follow a more devious course in consequence of the grog.

Even though the grog were porous the water would be continually flowing out of one medium into another and the rate of flow could not exceed that in the slow medium.

Grog does not improve the drying behavior in the water movement. The improvement comes from reduced shrinkage and from the fact that angular grog serves as an excellent binder to hold the mass together. Even though a crack should start on the surface it would quickly disappear against the grog aggregates. The ware might crackle and thus relieve the strain, but only excessive strain would develop an open crack.

The question arose as to whether the normally lower water content in a grogged clay was not a factor in the rate of flow. With Kentucky ball clay alone (curve 2) and with 20% grog and the same percentage of water (curve 1), the rate of shrinkage water flow was the same until the point of adsorbed water evaporation was approached, namely, to the break in the line. In the evaporation of adsorbed water within the mass, some advantage in favor of the grogged clay would be expected because of less shrinkage and greater openness of structure in consequence. In this abnormal grogged test, the rate of flow of shrinkage water was no faster than in the clay alone, and in all other tests the rate was slower in the grogged tests.

(6) Quantity of Water The Groveport clay (pugged soft) had a faster shrinkage water movement than that in a normal pug. The Tionesta fire clay (pugged soft) had a slower shrinkage water movement than in the normal pug. These tests, including the Kentucky clay test already described, are not conclusive, but they are indications which confirm the general results that the quantity of water is not a positive factor in the rate of shrinkage water flow.

In the rate of shrinkage water movement in the Kentucky clay, the Groveport clay (pugged soft), and the Michigan clay, the Bedford gray shale, and the Tionesta fire clay (pugged stiff) all come practically into the Kentucky clay shrinkage water stem. Plotted together, the maximum difference in any part of this stem does not exceed one and one-half hours.

In the waters of plasticity, these clays range from 19.6 to 40.8%. Two of them are bad in drying behavior, two are good, and one is fair, yet they all rank fast in shrinkage water movement.

Curve 3 in Fig. 1 is the Groveport clay normally pugged. It is exactly intermediate on the 18-gram line between the Texas clay (curve 5) and the Kentucky clay (curve 2).

Two other clays closely approximate this intermediate curve. The plasticity range is 18.7 to 26.6%.

It appears that the drying behavior of a clay can not be measured in terms of water of plasticity or by the rate of flow of shrinkage water.

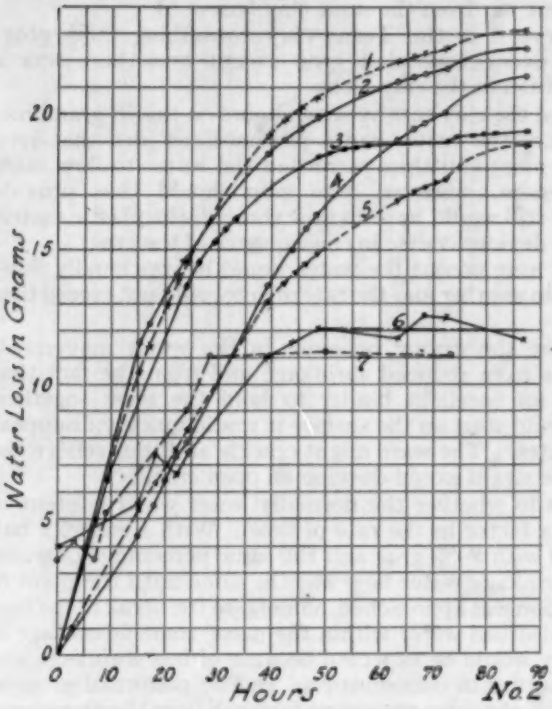

FIG. 2.

III. Effect of Chemical Treatment

Curve 2 in Fig. 2 is the "good" drying Bedford shale and curve 1 is this shale treated with HCl. The slight lag in the shrinkage water movement in the latter is negligible. In the "very bad" drying Michigan clay, the acid-treated test notably lagged (nine hours in the 18-gram line) the untreated clay. In this instance the acid-treated test closely approximated the grogged test. Though these two tests are not sufficient for a conclusion, they indicate that flocculation does not increase the rate of shrinkage water flow as has always been assumed.

The initial acidity or alkalinity of the clay must be considered in connection with acid treatment. Otherwise greater flocculation would be expected in the plastic Michigan surface clay than in the shale as well as greater change in rate of water flow; but a slower rate of flow was not anticipated. Acid treatment improves the drying behavior of many clays, but it is merely a palliative and not a corrective for drying. It is also less effective than the use of grog. If the results of these tests are confirmed then, since the improved drying condition due to the acid treatment is not caused by the increased rate of water flow, it is concluded that flocculation into aggregates increases the structural strength as does grog and makes the clay more resistant to shrinkage strains.

Curve 4 is the Bedford shale treated with a solution of sodium carbonate which compares with curve 2, and curve 5 is the Pennsylvania fire clay, similarly treated, which compares with the untreated Pennsylvania clay in curve 3.

However inconsistent the results of the grog and acid tests may seem, there is no inconsistency in the alkaline treatment. Clogged pores and slower water movement were expected.

If it seems inconsistent to blow hot and cold with the same breath, how then can slower shrinkage water flow with flocculation and deflocculation be reconciled? The explanation must lie in the character of the clay.

Fine-grained plastic clays are not necessarily high in dispersed colloidal clay. In such, the shrinkage water moves freely as several of the tests show. If the limited dispersed colloids are insufficient to clog the pores and capillary tubes, their flocculation would not invariably increase the rate of water flow. In some instances, the Michigan clay for example, there would be quite contrary results since coagulation would decrease the surface area upon which capillarity depends. Making the pores and tubes large and decreasing the number normally lessens capillarity.

These tests of the rate of water flow in clays under flocculation and deflocculation do not warrant final conclusions. From them and other tests, however, the opinion has been developed that the effect of electrolyte treatments depends upon the content and the state of the colloidal content.

If the content is low and not dispersed or but slightly dispersed, the Bedford shale for example, the effect of a coagulant will be slight or nil. The effect will increase with increased colloidal content and greater dispersion. In the first instance, there is no reason why the rate of flow of shrinkage water should advance, provided the rate is fast in the untreated clay. If the colloidal content of bentonite or Gumbo clays, for example, is high and dispersed to the degree that water movement in the untreated clay is slow, flocculation should increase the rate of flow.

(1) Alkalinity Tests Curves 6 and 7 show the alkalinity tests[3] of the Bedford shale and Pennsylvania fire clay with Na_2CO_3. The vertical scale of these curves is magnified compared with the scale of the other curves.

These tests, insofar as they go, confirm the assumption that the straight portion of the curves practically covers the water movement from the interior to the surface. In curve 6 (the Bedford shale test), there is evident overlapping of shrinkage water flow to the surface and adsorbed water evaporation below the surface as was suspected and previously mentioned.

(2) Kerosene Tests Fifteen bars from the various tests representing the clays (air, vacuum, and grogged tests) were placed on end in a shallow depth of kerosene. Though absorption by capillarity in the dry bars is not a perfect reversal of dewatering the wet bars because of the collapsed pores and capillary tubes through shrinkage, yet it is thought that they are related.

The rate of absorption varied widely. In some tests the liquid was up to the top of the four-inch bars in two days, and in other tests a longer time was necessary. It was nearly a month before the liquid came out fully to the top of the Texas clay bars.

[3] In the alkalinity tests, soda ash was dissolved in the pugging water, and at intervals in the drying one inch was cut from the drying end, slaked in water, and, after some time, titrated with dilute hydrochloric acid.

As the liquid rose in the bars, in some there was a sharp line between the dark solid wet lower belt and the light dry belt above. There was no intermediate belt of part saturation. In others there was a notable intermediate belt. The bars having these intermediate belts were made from the good drying clays and those with no intermediate bands were poor drying. The grogged clays showed no difference in the tests. If these intermediate belts mean anything favorable to good drying, then grog does not improve the drying behavior insofar as water flow is concerned, which conclusion had been reached before.

(3) Differential Flow These absorption differences are factors in drying behavior. If the water, as it drains out to the surface of the ware by capillarity, maintains a uniform level (no intermediate belt), the clay is probably bad in its drying behavior. Since shrinkage accompanies the drainage of shrinkage water (or would accompany it if not resisted) if there is no variable depth in the drainage, the successive layers or sections will be progressively subjected to the full force of the shrinkage strain. If it is assumed that drainage has advanced to a millimeter depth, then that thin section is subjected to the full strain of the shrinkage force. It can not, of course, at the moment actually shrink and it must structurally stretch until the compressive resistance has been moved some distance, when it will draw together.

If, on the other hand, the drainage is variable to a depth of one or more centimeters, the resistance to shrinkage is decreasing over this distance and the structural stretching is gradual. In other words, if the drainage of the shrinkage water is variable over considerable depth, the drying section has ample opportunity to adjust itself to the strains which otherwise would cause cracking.

Such variable flow may be designated as "differential flow" of the shrinkage water.

IV. Conclusions

(1) The water in a stiff-mud ware flows to the surface by capillarity at a constant rate until about 60% is eliminated. This is shrinkage water.

(2) The adsorbed water is removed by evaporation within the ware. Undoubtedly there is more or less overlapping of the shrinkage water loss and of the adsorbed water loss.

(3) Structure is a factor as shown by the slower movement of the shrinkage water in hand-molded tests. By analogy, water movement will be slower across than along lamination planes.

(4) Grog in the clay lessens the rate of flow of the shrinkage water. If a fast rate is essential, grog is not an aid. Its benefit comes from less shrinkage and greater binder action.

(5) Flocculating with acid in a normal clay does not increase free flow of the shrinkage water. Flocculation will be beneficial in a clay so highly colloidal that the pores and capillary tubes are clogged with colloids.

(6) Deflocculation retards the flow of the shrinkage water.

(7) Vacuum treatment to eliminate the air has little effect on the rate of shrinkage of water flow.

(8) There is no relation between the plasticity and quantity of water of plasticity and the rate of flow of shrinkage water. The most plastic and one of the least plastic, together with intermediate degrees of plasticity, were fast in rate of shrinkage water flow.

A decidedly plastic and the least plastic were intermediate in rate of flow. The clay with the slowest rate of flow was plastic, but slightly less so than two other plastic surface clays which ranked intermediate and fast in rate of water flow.

(9) There is no relation between drying behavior and rate of water flow. Good and bad drying clays were found in both the fast and medium classes.

That plastic clays are prone to bad drying behavior is a coincident. They lack the structural factors such as binder aggregates, and they have higher shrinkages.

(10) The kerosene tests indicate that "differential flow" of the shrinkage water may be a contributing factor or even a major factor in drying behavior. Complete saturation advanced in level stages in the bad drying clays (including grogged bad drying clays), whereas in the good drying clays the degree of absorption tapered off in advance of complete saturation. There was no relation between the rate of absorption and the drying behavior, though in a measure the rate of absorption correlated with the rate of flow of shrinkage water in the initial tests.

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PAPERS FROM THE SECOND SYMPOSIUM ON THE PHYSICAL CHEMISTRY OF THE ALUMINA-SILICA REFRACTORIES*

R. B. Sosman, *Chairman*

I. THE ROLE OF SILICON AND ALUMINUM IN COMPLEX SILICATES

By B. E. Warren

Introduction

During the last six years the crystal structures of a large number of silicates have been determined by the methods of X-ray diffraction. This work, which is largely due to W. L. Bragg[1] and his school, has given a new physical chemistry of silicates sufficiently well founded to permit many general conclusions regarding the nature of silicates and the rôle played by the component atoms. The methods which have been used in working out the structures of complex silicates are of course too involved to be considered here in detail, and the writer will present only a discussion of the results and of the general conclusions to be drawn.

Silicon Atom

In all of the silicate structures so far analyzed, the silicon atom has been found surrounded by four oxygens arranged at the corners of a tetrahedron, with a very constant silicon-oxygen distance of about 1.6 times 10^{-8} centimeters. The bonding between silicon and oxygen is probably a combination of ionic and homopolar bonds, the combination resulting in a bond which is very strong compared with other bonds which exist in silicates. In the various forms of silica these Si-O bonds run unbroken in all directions throughout the crystal, and the relatively high melting point and hardness of silica is a direct indication of the strength of the silicon-oxygen bond.

Olivine

In a simple orthosilicate such as olivine (Mg_2SiO_4) independent SiO_4 groups are found, and these groups play essentially the same rôle in the structure as, for example, the tetrahedral SO_4 group in a sulfate crystal. When the oxygen-to-silicon ratio becomes less than 4, complex silicon-oxygen groups are formed in which each silicon is still tetrahedrally surrounded by four oxygens, but part of the oxygens are shared between two tetrahedral groups. For example, when the silicon-to-oxygen ratio is 2:7, Si_2O_7 groups are found in which the two SiO_4 tetrahedra are sharing one oxygen between them. In the pyroxenes where the silicon-oxygen ratio is 1:3 the structure is found to contain long chains of silicon-oxygen tetrahedra, each tetrahedral group linked to its neighbor on either side by a shared oxygen. In the asbestos compounds with a Si_4O_{11} composition, double chains are formed, and in the micas where the effective composition is Si_2O_5 the tetrahedral groups are linked together in two dimensions to form

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* The following papers have been submitted for the Second Symposium on the Physical Chemistry of the Alumina-Silica Refractories, at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Refractories Division). Received June 21, 1933.

For the papers in the First Symposium see *Jour. Amer. Ceram. Soc.*, **16** [1], 54–76 (1933). Other papers are in preparation.

[1] W. L. Bragg, "The Structure of Silicates," *Z. Krist.*, **74**, 237 (1930).

endless sheets. It is just this possibility of building up extended silicon-oxygen complexes which differentiates the physical chemistry of silicates from that of the salts of typical inorganic acids. This tetrahedral grouping of four oxygens about each silicon under the action of the strong Si-O bond represents so strong a tendency that it will be carried out regardless of other atoms present, and it is certainly the predominating factor in determining the crystal structure of silicates. Except in orthosilicate compositions this tendency to form complexes must also be present in the melt and must be closely related to the ease with which silicates form glasses.

Rôle of Aluminum Atom

The aluminum atom plays a more complicated rôle in alumino-silicate structures. It is usually found symmetrically surrounded by six oxygens at a distance of about 1.9 times 10^{-8} centimeters. In some structures it is found tetrahedrally surrounded by four oxygens similar to silicon. In the single case of andalusite, Al_2SiO_5, it appears to be quite definitely established that one-half of the aluminum atoms are surrounded by five oxygen atoms. In some cases within a single structure, the aluminum is present partly in one fashion and partly in the other. In many complex silicates, such as the hornblendes (asbestos) and mica, part of the positions in the structure allotted to silicon are occupied by aluminum or, in other words, aluminum is substituting for part of the silicon.

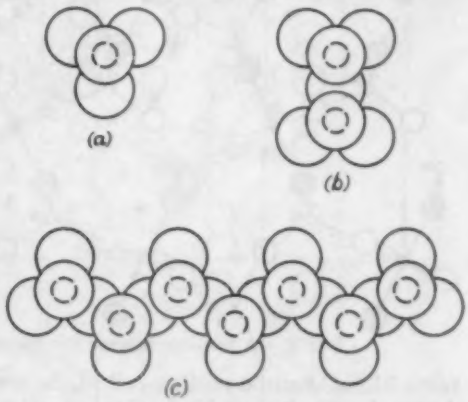

FIG. 1.—Types of silicon-oxygen groups. (*a*) SiO_4 groups in orthosilicates; (*b*) Si_2O_7 groups; (*c*) SiO_3 chains in pyroxenes.

The rôle played by water in alumino-silicates is also a rather varied one. However, in most of the materials of ceramic interest the water (if actually combined) is present as hydroxyl (OH). In no structure so far analyzed have these (OH) groups been found bonded to the silicon. They are always found surrounding other atoms such as Al, Mg, Ca, etc.

Cyanite-Andalusite-Sillimanite

The alumino-silicates, namely cyanite, andalusite, and sillimanite, have been discussed in detail in a paper by W. H. Taylor.[2] The composition is the same for all three substances, Al_2SiO_5. In each of the three structures, half of the aluminums are surrounded in the usual way by six oxygens, while the other half of the aluminums are surrounded by six oxygens in cyanite, five in andalusite, and four in sillimanite.

At high temperatures sillimanite ($Al_2O_3 \cdot SiO_2$) changes over into mullite $3Al_2O_3 \cdot 2SiO_2$. X-ray diffraction patterns of sillimanite and mullite are so nearly identical that it requires rather careful scrutiny of the patterns to differentiate between them. Hence so far as X-ray scattering is con-

[2] W. H. Taylor, see the paper following in this *Journal*, p. 418.

cerned, the structures of these two substances must be very nearly the same. As pointed out by several workers, the unit cell of sillimanite con-

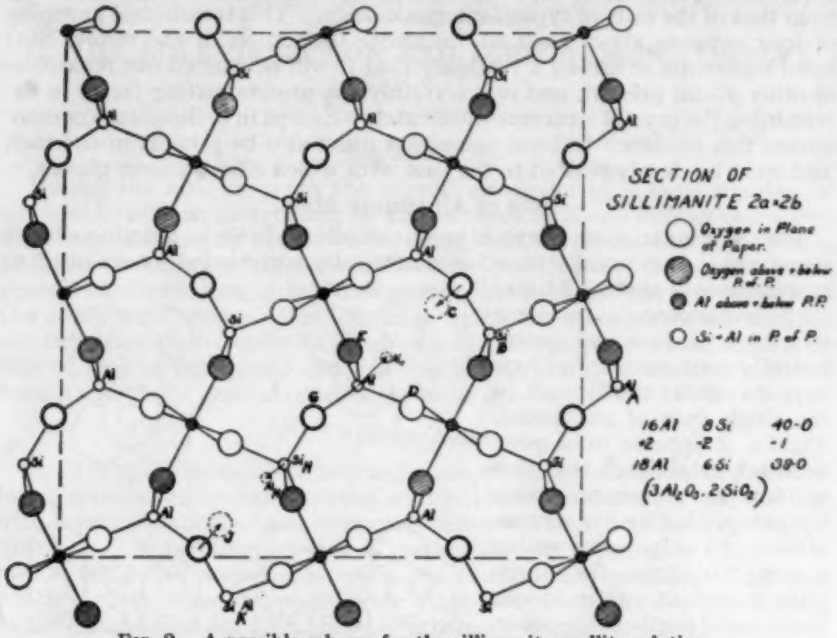
SECTION OF
SILLIMANITE 2a×2b
Oxygen in Plane of Paper.
Oxygen above + below P. of P.
Al above + below P.P.
Si + Al in P. of P.
16 Al 8 Si 40-0
+2 -2 -1
18 Al 6 Si 39·0
(3Al2O3.2SiO2)

FIG. 2.—A possible scheme for the sillimanite-mullite relation.

tains $Al_9Si_4O_{20}$ and a mullite cell of the same size would contain $Al_9Si_3O_{19^1/_2}$. As Taylor has pointed out, since aluminum forms tetrahedral groups similar to silicon, it can be imagined that in each sillimanite cell one silicon is replaced by aluminum and then to balance valencies one oxygen in every forty is left out.

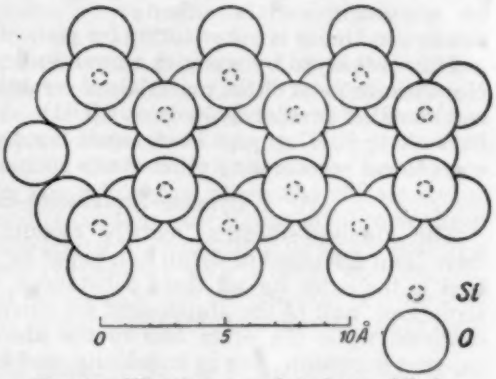

FIG. 3.—Silicon-oxygen chain in amphibole.

There seems to be no reason for doubting that the main features of this scheme are correct. When examined in detail, however, the problem still has a few points that are rather puzzling. The removal of one oxygen in forty will be tolerated by the structure if some of the other oxygens which are bonded to only two cations are slightly displaced so that they are now shared between more than two groups, therefore effectively substituting for the missing oxygen. Taylor[3] has

[3] W. H. Taylor, "Structure of Sillimanite and Related Materials," *Jour. Soc. Glass Tech.*, **16**, 111 (1932).

proposed a mechanism for the change, but since it involves an oxygen being shared between four aluminum atoms in tetrahedral coördination and therefore gives it a valence bonding of $4 \times {}^{3}/_{4} = 3$, it seems to be rather unlikely.

A scheme which appears to be more reasonable would involve a displacement of the oxygens in such a way that those taking on additional bonding would be shared between three aluminum atoms in tetrahedral groups. The possibility of such a change is seen in Fig. 2 which represents a section of the

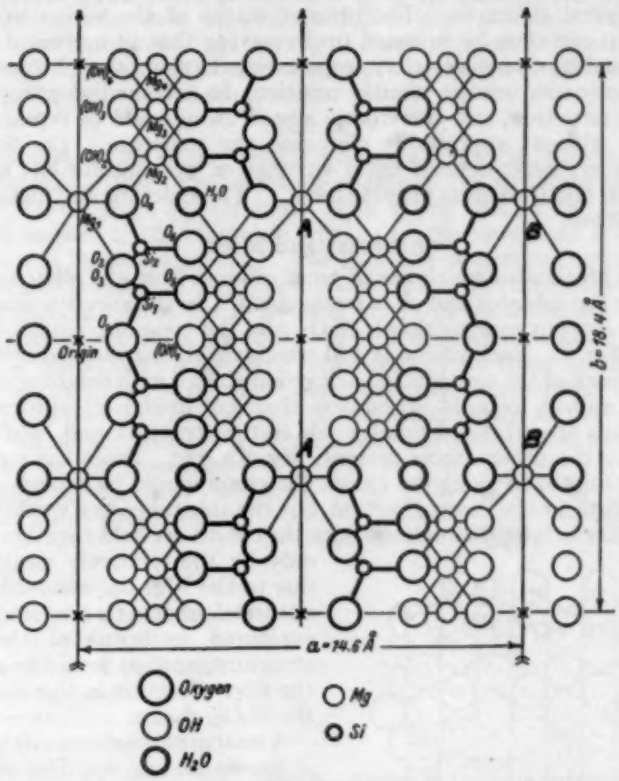

FIG. 4.—Projection of chrysotile structure perpendicular to c-axis.

sillimanite structure $2a$ by $2b$ by $\frac{c}{2}$. Oxygens C and J are displaced slightly as indicated, and oxygen G is removed from the structure. Al (F) is then displaced as indicated into the new tetrahedral group formed with oxygen C. Si (H) is replaced by Al (H) displaced into the new group formed with oxygen J. Finally, Si (K) is replaced by an Al, and Si (B) exchanges places with any neighboring Al. In the section of sillimanite structure which originally comprised $Al_{16}Si_8O_{40}$, one oxygen and two silicons were removed and two aluminums were introduced so that the new content is $Al_{18}Si_6O_{39}$ or $3(3Al_2O_3 \cdot 2SiO_2)$.

Although some such scheme as the one above proposed would be a reasonable one, as far as all empirical rules for silicate structures are concerned, it is nevertheless not a satisfactory final answer. There is no reason why the proposed change should take place just once in every structure-unit $Al_{16}Si_8O_{40}$, and the resulting configuration does not represent a definite crystal structure. Hence there would be no reason to expect a definite mullite composition.

The available evidence seems to indicate that mullite does have a fairly definite chemical composition, and hence it is supposed that it has a definite crystal structure. The present status of the sillimanite-mullite relationship can then be summed up by saying that in a general way the relation must be essentially that proposed by Taylor; the silicons and half of the aluminums occupy similar positions in tetrahedral groups in the sillimanite structure, and therefore a silicon atom could be replaced by an aluminum without appreciably changing the structure. The final solution, however, must depend upon whether or not mullite has a definite composition and if so must provide for it. These details still await a satisfactory answer.

Asbestos and Mica

A group of silicates which are of great interest from the structural point of view are the asbestos and mica compounds. In the asbestos compounds[4] the silicon-oxygen composition is Si_4O_{11} and the type of complex formed is shown in Fig. 3. Each silicon is still tetrahedrally surrounded by four oxygens with part of the oxygens in each group shared with neighboring groups in such a way as to build up endless chains of linked tetrahedral groups. These chains are arranged side by side in the structure and held together laterally by the other atoms present, Mg, Ca, etc. Since the strong Si-O bonds run unbroken along the chain, the chain would be expected to have great strength in the chain direction, but the substance as a whole would be much weaker in lateral directions since the chains are held together laterally only by the relatively weaker bonds due to the Mg, Ca, etc. The fibrous nature of asbestos is thus immediately explained in terms of the crystal structure, and, as would be expected, the fiber direction is the direction of the Si_4O_{11} chains.

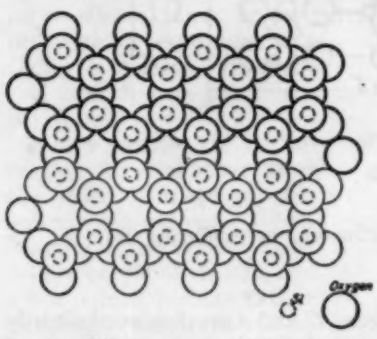

FIG. 5.—Silicon-oxygen sheet as in mica.

A section of the chrysotile[5] structure is shown in Fig. 4. The chains run perpendicular to the plane of the paper and are outlined in cross-section somewhat heavier. Each Mg is octahedrally surrounded by 6 anions (oxygen or hydroxyl), in much the same way as in brucite, $Mg(OH)_2$. The chrysotile structure is essentially Si_4O_{11} chains cemented together side-wise by layers of brucite. It is of interest to note that each hydroxyl is bound to three equidistant Mg atoms and is displaced appreciably from the plane of these three, in keeping with the dipole character of

[4] B. E. Warren, "Structure of Asbestos," *Ind. Eng. Chem.*, **24**, 419 (1932).
[5] B. E. Warren and W. L. Bragg, "Structure of Chrysotile," *Z. Krist.*, **76**, 201 (1930).

the (OH) groups. Across large sections such as *AA* and *BB* no direct bonds operate, and the structure is held together only by weak secondary forces. Therefore it would be expected that chrysotile would be readily fibered and that the fibers would be quite flexible.

The crystal structure of the micas[6] is closely related to that of the asbestos compounds. A silicon-oxygen complex, Si_2O_5, is built up which is similar to the chain in asbestos except that it is endless in two dimensions rather than one and hence forms a sheet. The Si_2O_5 sheet in mica and its relation to the Si_4O_{11} chain in asbestos is shown in Fig. 5. The crystal structure of mica is made up of these silicon-oxygen sheets, stacked one upon the other, and held together by the other atoms present: Al, Mg, OH, K, etc. The flaky character of mica is of course a direct consequence of the Si_2O_5 sheets out of which is built.

Kaolin

The crystal structure of the kaolins is again a sheet structure very similar to that of mica. Figure 6 represents a section of the structure of kaolinite $(OH)_4Al_2Si_2O_5$ as given by Gruner.[7] The upper half of the layer is an Si_2O_5 sheet similar to that found in mica, and the lower half is a layer of aluminum and hydroxyl groups. The kaolinite structure comprises such layers stacked parallel to one another and held together only by weak secondary forces. Since the individual layers in kaolinite are not symmetrical, that is, an Si_2O_5 sheet on one side and an aluminum hydroxyl sheet on the other, there might well be a tendency for these sheets to curve since the two parts might not have quite the same dimensions. This may be the explanation for the fact that kaolin occurs only as tiny flake-like crystals. The other forms of kaolin are built up out of these same double sheets, and differ from one another only in the way in which one sheet packs upon the next.

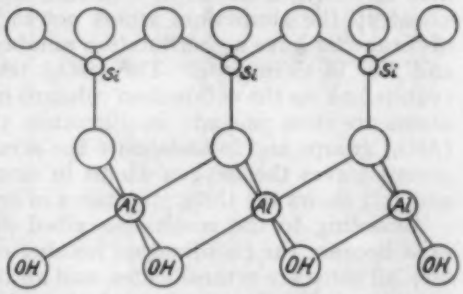

FIG. 6.—Section of the layer structure of kaolinite $(OH)_4Al_2Si_2O_5$.

Conclusion

These examples should serve to illustrate the extent to which the physical properties of complex silicates in terms of their crystalline structure as derived from X-ray diffraction analysis can be understood and interpreted. Whereas a few years ago, X-ray diffraction analysis of ceramic materials could be used only in identifying various compounds present, it is today rapidly approaching the stage where the complete structure determination permits an understanding of the physical properties of the material and, what is perhaps even more important, it is building up a new and well-founded physical chemistry of the complex alumino-silicates.

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[6] L. Pauling, "Structure of the Micas and Related Minerals," *Proc. Nat. Acad. Sci.*, **16**, 123 (1930); Jackson and West, "Structure of Muscovite," *Z. Krist.*, **76**, 211 (1930).

[7] J. W. Gruner, "Crystal Structure of Kaolinite," *ibid.*, **83**, 75 (1932).

II. STRUCTURE OF SILLIMANITE AND RELATED MATERIALS

By W. H. Taylor

Introduction

The methods of X-ray analysis have been applied to determine the structures of the three naturally occurring forms of Al_2SiO_5 (cyanite, sillimanite, and andalusite), and some progress has been made toward the complete explanation of the relationship between sillimanite and mullite. The present paper includes a brief account of the main features of the three structures, and a discussion of the sillimanite-mullite relationship.

Cyanite, Sillimanite, and Andalusite

Cyanite is triclinic, sillimanite and andalusite are orthorhombic with unit cells of the same size and shape, and all three unit cells contain the same number of atoms, that is, four molecules of the composition Al_2SiO_5. It is found[1] that all three structures are built up around continuous columns of octahedral groups of oxygen atoms; each octahedron contains an aluminium atom and shares one edge with the octahedron above and one edge with the octahedron below. As a consequence of this feature of the structures, the length of the *c* axis in each of the three crystals is about 5.7*A*. Figure 1 (*d*) shows the positions of the columns in the three crystals, other atoms in the unit cells being omitted from the diagram.

The columns of octahedra contain one-half of the aluminium atoms in the unit cell, and the silicon atoms and remaining aluminium atoms link the columns together laterally. In all three structures each silicon atom is inside a tetrahedral group of oxygen atoms, and these SiO_4 groups do not hold any oxygen atoms in common, so that all three crystals are orthosilicates; the aluminium atoms not included in the continuous columns of octahedra have a coördination number *six* in cyanite, *five* in andalusite, and *four* in sillimanite. The (SiO_4) tetrahedra and (AlO_6) octahedra in cyanite link up the octahedron columns in such a way that all of the oxygen atoms are close packed; in sillimanite the arrangement of the (SiO_4) and (AlO_4) groups and in andalusite the arrangement of the (SiO_4) and (AlO_5) groups leaves the oxygen atoms in more open array. Figure 1((*a*), (*b*), and (*c*)) shows the three structures in detail.

According to the results described above, the three forms of Al_2SiO_5 exist because the coördination number of aluminium may be four, five, or six; all three are orthosilicates, and all three structures are based on an arrangement of columns of octahedra which may explain the more or less fibrous nature of the minerals. The especially fibrous character of sillimanite is probably due to the existence of strings parallel to the *c* axis of alternate (SiO_4) and (AlO_4) tetrahedra.

Sillimanite and Mullite

The author's contribution[2] toward a solution of the problem of the relationship between sillimanite and mullite is based on the determination of

[1] St. Náray-Szabó, W. H. Taylor, and W. W. Jackson, Cyanite, *Z. Krist.*, **71**, 117 (1929); J. S. Hey and W. H. Taylor, Sillimanite and Andalusite, *ibid.*, **80**, 428 (1931).

[2] (*a*) W. H. Taylor, Sillimanite and Mullite, *Z. Krist.*, **68**, 503 (1928); (*b*) W. H. Taylor, *Jour. Soc. Glass Tech.*, **16**, 111 (1932); (*c*) W. H. Taylor, "The Crystal Structure of Sillimanite and Related Materials," *Trans. Ceram. Soc.* [Eng.], **32** [1], 7 (1933).

the sillimanite structure. The unit cell of sillimanite contains $Al_8Si_4O_{20}$ or $Al_4(Si_4Al_4)O_{20}$—bracketing together silicon and aluminium atoms which are contained in tetrahedral groups of oxygen atoms—and there is a very marked pseudo-cell one-half this size (*i. e.*, with the *c* axis about 2.8*A*). The unit cell of mullite is apparently almost identical with this pseudo-

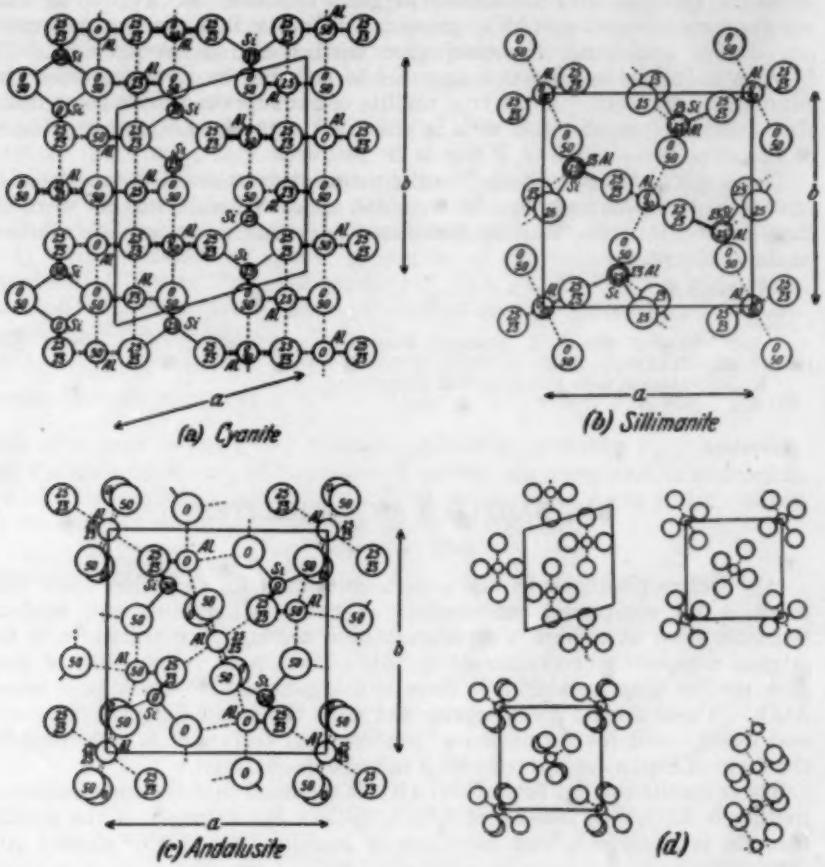

FIG. 1 (*a*), (*b*), and (*c*).—The structures of cyanite, sillimanite, and andalusite, viewed along the *c* axis.
FIG. 1 (*d*).—Key diagram showing the positions of the columns of octahedra.
The heights of the atoms are given as percentages of the length of the *c* axis (5.7*A*).

cell, and if the chemical composition is $3Al_2O_3{\cdot}2SiO_2$ or $Al_6Si_2O_{13}$, it must contain $Al_{4^1/_2}$, $Si_{1^1/_2}$, $O_{9^1/_4}$ as was first stated by Wyckoff, Greig, and Bowen.[3] The intensities of corresponding X-ray reflections from the two crystals are almost but not quite identical. Assuming the chemical composition to be given correctly, the problem is to explain why two crystals with different compositions give very similar X-ray diffraction patterns, and why

[3] R. W. G. Wyckoff, J. W. Greig, and N. L. Bowen, Sillimanite and Mullite, *Amer. Jour. Sci.*, 5th Ser., **11**, 459 (1926).

the unit cell of mullite contains only a fraction of a molecule ($^3/_4$ of $Al_6Si_2O_{13}$). The author suggests that the explanation may be based on the similarity of the (SiO_4) and (AlO_4) groups. The sillimanite unit cell contains $Al_4(Si_4Al_4)O_{20}$, and the (SiO_4) and (AlO_4) groups alternate in the direction of the *c* axis; a mullite cell of the same size contains $Al_9Si_3O_{19^1/_2}$ or $Al_4(Si_2Al_5)O_{19^1/_2}$, and the author suggests that one (SiO_4) group in sillimanite is replaced by an (AlO_4) group in mullite, so that the two structures are similar and must therefore give similar diffraction patterns. To balance valencies one oxygen atom in forty must be removed from the sillimanite structure. If the true mullite cell is supposed to be larger than the observed (pseudo) cell, this is possible[2b] without serious disturbance of the structure.

These speculations are based on the assumption that the composition of mullite is $Al_6Si_2O_{13}$, and must be regarded as provisional: further work by Bradley and Roussin,[4] and by Nahmias,[5] may lead to a complete solution of the problem.

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[4] A. J. Bradley and A. L. Roussin, Porcelains and Mullite, *Trans. Ceram. Soc.* [Eng.], **31**, 422 (1932).
[5] M. E. Nahmias, note following this paper.

III. BAUXITES AND MULLITES*

BY M. E. NAHMIAS

(1) Debye photographs taken with chromium K_α radiation show that there is no compound intermediate between sillimanite and mullite. Bauxites fired at a high temperature give mullite plus tridymite if the original composition corresponds to $3Al_2O_3{\cdot}2SiO_2$ plus excess SiO_2, or they give mullite plus corundum if there is originally $3Al_2O_3{\cdot}2SiO_2$ plus excess Al_2O_3. These results are in agreement with the phase-diagram of Bowen and Greig,[1] and the formation of mullite plus tridymite is confirmed by the form of expansion curves which have been obtained.[2]

These results can not be explained if it is assumed that the composition of mullite is $Al_2O_3{\cdot}SiO_2$ instead of $3Al_2O_3{\cdot}2SiO_2$. For example, if the mullite formula is $Al_2O_3{\cdot}SiO_2$, one specimen of bauxite (No. 4718)[3] should give

* This note is an extract from a paper published in *Zeitschrift für Kristallographie*, (A) **85**, 355 (1933). Received June 21, 1933.

[1] N. L. Bowen and J. W. Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238–54 (1924); see also errata, **7** [5], 410 (1924).

[2] The author has repeated the experiments of Heindl, Pendergast, and Mong (Bur. Stand., *Jour. Research*, **8** [2], 199–215 (1932)) but has never found an $\alpha \longrightarrow \beta$ cristobalite transformation occurring below 210 °C (Chevenard apparatus, Pellin, Paris, with which $\alpha \longrightarrow \beta$ quartz occurs at 575 °C ± 5°).

[3] Bauxite 4718 (calcined product) contains 58% Al_2O_3, 33% SiO_2; if the mullite formula is $Al_2O_3{\cdot}SiO_2$, then the ratio $\frac{Al_2O_3}{SiO_2} = 1.66$ and all of the silica present combines with 54% of Al_2O_3, leaving 4% free Al_2O_3; if the formula is $3Al_2O_3{\cdot}2SiO_2$, then the ratio $\frac{Al_2O_3}{SiO_2} = 2.54$ and all of the alumina present combines with 23% of silica, leaving 10% of free silica.

mullite plus corundum, whereas it actually gives mullite plus tridymite, as is to be expected if the mullite formula is $3Al_2O_3 \cdot 2SiO_2$.

(2) The SiO_2 in bauxites is present as a constituent of kaolinite, and the excess Al_2O_3 is principally in the form of boehmite ($Al_2O_3 \cdot H_2O$). Therefore heat treatment at 450° results in the formation of free γAl_2O_3 and free amorphous SiO_2. The same products are formed if the temperature of heat treatment is raised as far as 950° when some mullite lines first appear in powder photographs; above this temperature the mullite structure becomes more and more definite, and material treated at 1100° gives the complete mullite X-ray pattern.

Neither $4Al_2O_3 \cdot 3SiO_2$ nor $Al_2O_3 \cdot 2SiO_2$ is formed from kaolinite, for bauxites containing only hydrates of alumina give the same pattern of γAl_2O_3 above 450° as is given by bauxites containing much kaolinite. No sillimanite is formed at about 700° (as was proposed by Hyslop and Rooksby[4] in their scheme for the transformation of kaolinite into mullite).

(3) The variation in optical properties of different mullites has been explained[5] as due to the solid solution of TiO_2 and Fe_2O_3; the differences observed in Debye photographs of various mullites may perhaps be explained in the same way.

(4) Debye photographs and rotation photographs of mullite give approximate axial lengths $a_1 = a$, $b_1 = b$, and $c_1 = \frac{c}{2}$, where a, b, and c are the axial lengths of sillimanite[6]; the space group is probably V_h^1. Assuming that the accepted chemical formula and density are accurate it is impossible to find a structure in conformity with this unit cell and space group; either the density or the chemical formula needs adjustment.

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[4] Hyslop and Rooksby, *Trans. Ceram. Soc.* [Eng.], **27**, 93–96 (1928).
[5] N. L. Bowen, J. W. Greig, and E. G. Zies, *Jour. Wash. Acad. Sci.*, **14**, 191 (1924).
[6] W. H. Taylor, *Z. Krist.*, **68**, 504 (1928).

IV. DISCUSSION ON THE PHYSICAL CHEMISTRY OF THE ALUMINA-SILICA REFRACTORIES

RALPH W. G. WYCKOFF (communicated discussion): In a recent paper Bradley and Roussin[1] have published a series of X-ray powder photographs which have been thought to show that the principal crystalline constituent of porcelains is not mullite, $3Al_2O_3 \cdot 2SiO_2$, but "porzite," a substance of undetermined composition. Since this conclusion is so much at variance with other information it is important to realize that there may be an alternative explanation of the X-ray data.

To a considerable extent the early uncertainty as to whether mullite and sillimanite have identical diffraction patterns[2] was due to the fact that these minerals when ground cleave into rod-like or fibrous masses. It is very hard to destroy the preferred orientations in these masses even after the individual particles have become so small that the powder patterns are entirely free from large crystal streaks. For this reason either of these compounds will yield perfect-appearing photographs which differ from one another in the relative intensities of certain of their reflections.[3] The published photographs attributed to mullite and to "porzite" differ in exactly this way.

It seems unlikely that the differences in pattern found by Bradley and Roussin can be ascribed to solid solutions involving the two constituent oxides, and it is most rational in the light of the data thus far published to consider them as due to different degrees of preferred orientation of mullite crystals in the mineral and porcelain samples photographed.

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[1] Bradley and Roussin, *Trans. Ceram. Soc.* [Eng.], **31**, 422–30 (1932).

[2] Wyckoff, in Bowen and Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238 (1924) and **7** [5], 410; Norton, *ibid.*, **8**, 401 (1925); Navias and Davey, *ibid.*, **8**, 640 (1925); Wyckoff, Greig, and Bowen, 5th Ser., *Amer. Jour. Sci.*, **11**, 459 (1926).

[3] Wyckoff, Greig, and Bowen, *op. cit.*

DISCUSSION ON "THEORY OF SPALLING"*

By F. H. Norton

This reply to Dr. Preston's discussion of the paper on the "Theory of Spalling" by the writer is presented with the purpose of showing (1) that this mathematical theory is correct as based on given assumptions, and (2) that these assumptions are reasonable from physical evidence.

Preston admits that there are shearing stresses in solids when they are subject to an uneven temperature distribution. This is proved by photoelastic studies, by the type of fracture, and by the simplest application of the theory of elasticity. No attempt has been made in this theory to compute either the magnitude or the direction of the shear stresses, but only their interrelation to certain fundamental properties of the refractory. It is interesting to note that such well-known scientists as M. T. Huber,[1] H. Hencky,[2] and R. Mises[3] go further than the writer. They believe that all fractures are due to shearing stresses.

In Dr. Preston's discussion he attempts to show by means of the illustration in Figs. 1 to 3 that no shear occurs. What he says is true, but it does not apply to the case of a heated solid as considered in the writer's theory. The terminal couples shown in Fig. 3 to straighten the curved bar would be present only to a minor extent, but the main straightening factors are the tension forces normal to the bar along the center which would, of course, introduce shear. His illustration properly interpreted is an excellent proof of the presence of shear. Again, Dr. Preston has to assume a uniform temperature gradient to eliminate shear in his illustration, and this would almost never occur in a solid suddenly heated or cooled.

Dr. Preston is quite right when he says that shear occurs at 45° to the principal stress and is equal to one-half the algebraic difference of the principal stresses.

Note: This statement was made in the writer's book, Refractories, on page 340, paragraph 4.

In the theory under discussion, however, we are concerned with a solid where the distribution of stress is very complex and can be worked out analytically only in a few of the simpler cases. In the writer's theory it was attempted to obtain only the relation between the shearing stress at a given point and the physical properties of the body. The theory does not attempt to prove in itself that failure is due to shear or to determine the actual magnitude or the direction of the stresses.

In the example shown in the writer's book, the shear stresses are parallel to the isothermal as developed in the theory, but it is clear that in larger sections or in the case of a sphere the lateral expansion of the outer layer will be restrained, not only by the shearing stress parallel to the surface but also by the compression stress which reacts nearly parallel to the surface. This, in fact, may rotate the direction of shear, but the same relation will apply between shearing stress and physical properties of the body.

In regard to the comparison between the writer's formula and that of

* This discussion is a reply to a paper by F. W. Preston published in *Jour. Amer. Ceram. Soc.*, **16** [3], 131 (1933). Received March 22, 1933.

[1] M. T. Huber, Die Spezifische Formänderungsarbeit als Mass der Anstrongung eines Materials. Lemberg (1904).

[2] H. Hencky, *Z. angew. Math. und Mech.*, Vol. 4, No. 4 (1924).

[3] R. Mises, Göttinger Nachrichten, 1913, pp. 582–92.

Winklemann's, there is a factor of size in the former which does not occur in the latter. This factor becomes a nondimensional constant when pieces of similar shape and size are compared, which condition was stated by the writer.

In comparing objects of different size there are complications, since we may have either a similar temperature distribution, in which case the gradient at any point will be inversely proportional to the size, or we may have gradients produced by equal surface conditions. In the latter case the stresses must increase with the size. This is substantiated by the well-recognized fact that large objects fracture more readily than small ones on heating or cooling.

In conclusion, Dr. Preston will perhaps be interested in one of the important modern developments in the field of refractories, the Radex magnesite brick, which has a remarkable resistance to spalling. This brick was developed in Germany by Dr. Endell,[4] who was kind enough to state that the writer's formula was used in this investigation, and gave excellent agreement with the experimental results. He brings out clearly that a spall-resisting brick must have a high shear flexibility.

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[4] K. Endell, "Gegen Temperaturänderungen unempfindliche Magnesitsteine," *Stahl Eisen*, 31 [52], 759–63 (1932); Zur Berechnung der Temperaturwechselleständigkeit feuerfester Steine ausichren physikalischen Honstanten. Glastechnischen Tagung, January, 1933.

GASES IN GLASS*

By R. H. Dalton

ABSTRACT

An apparatus is described for extracting the gas from glass at glass-furnace temperature and determining its composition. Results are given for glasses of various compositions and various melting histories. All ordinary glasses were found to contain appreciable quantities of dissolved (or chemically combined) gas, the amount varying from a few hundredths to a few tenths per cent. Water is frequently the most abundant gas, the content being highest in borosilicate glasses. Carbon dioxide is also usually present, the amount depending on the basicity of the glass. Nitrogen, carbon monoxide, and hydrogen were never found present in appreciable quantities. All oxidized glasses contain some oxygen. Glasses containing arsenic give off a comparatively large volume of oxygen. The effect of this oxygen on fining is discussed. It has been found that remelting a glass has little effect on the gas content. The gas content is greatly influenced by the size of the melt, being the lowest in small experimental melts.

I. Introduction

This paper deals with the first part of some work that has been in progress in the laboratory of the Corning Glass Works for the last three years. The object of the investigation has been (1) to develop an apparatus for extracting and analyzing the gas from glass at melting temperatures; (2) to determine the effect of gas on the properties of the glass and on fining; and (3) to study the equilibria of gases in contact with molten glass.

The present paper deals almost entirely with the first of these topics including the results of some typical analyses.

It is a well-known fact that all ordinary glasses contain gas. This is frequently brought out in the difficulties which arise in connection with fining and with the use of glass as a vacuum container. It has also been pointed out by various investigators, most of whom, however, have confined their observations to temperatures below the softening point. It is beyond the scope of this paper to discuss these investigations in the low-temperature region. The earliest work at high temperatures was that of E. S. Shepard mentioned in an article by Allen and Zies.[1] This was followed by the more extensive work of Washburn, Footitt and Bunting.[2]

Both of these investigations, however, failed to provide for the detection and estimation of water vapor. A more complete investigation has been reported recently in a series of three articles by Salmang and Becker.[3]

The present work is in general agreement with theirs. The number of factors that influence the results are so great, however, that close quantitative agreement can not be expected. Also the field is so new that it is more important to explore a large number of glasses than to work out refinements in the procedure in an attempt to push the accuracy to the limit.

Before proceeding to a description of the apparatus and methods of the present investigation it is of interest to get a general idea of the volume of gas to be measured and of the relation of dissolved gas to that in other forms. If an ordinary piece of glass is heated in a vacuum, gases begin to be evolved almost immediately. The extent of the evolution depends of

* Received May 23, 1933.

[1] E. T. Allen and E. G. Zies, *Jour. Amer. Ceram. Soc.*, 1 [11], 739 (1918).

[2] Washburn, Footitt, and Bunting, Univ. of Ill. Eng. Expt. Sta., *Bull.* No. 118 (1920).

[3] H. Salmang and A. Becker, *Glastech. Ber.*, 5, 520 (1928); 6, 625 (1929); 7, 241 (1930).

course on the temperature. Figure 1 shows, in a general way, the gas volumes evolved at various temperatures for a sample of glass 1 by 1 by 0.1 centimeter. The low foot at the beginning of the curve is due to the gas at or near the surface of the glass that comes off below the softening point. At high temperatures where flow in the glass becomes possible, the dissolved or chemically combined gases come off. The intermediate section of the curve is dotted to indicate that there are no actual observations in that neighborhood. The dissolved gases are of the order of 100 times the volume of the surface gases if the sample is heated to glass furnace temperatures. In the present work the glass is introduced into an evacuated furnace at about 1400°C; so it is the total gas that is being measured, both dissolved and from the surface. The latter is a very small percentage of the total. Any gas present in bubbles would also be included although this again is a very small contribution. The bubbles even in a very "seedy" sample would not be more than 1% of the dissolved gas. It should be mentioned that the term "dissolved gas" includes all gas obtained from the glass phase regardless of whether it be physically dissolved or chemically combined. To permit ready comparison a table of volumes of gas in the different forms has been included in Fig. 1.

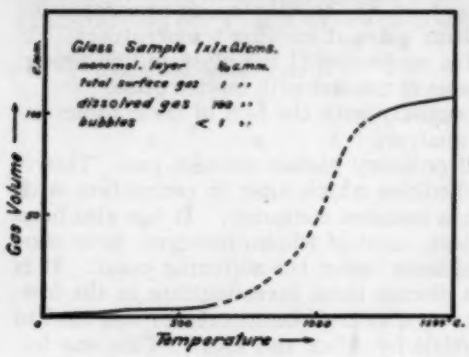

FIG. 1.

II. Apparatus and Procedure

The vacuum furnace for extracting the gases from glass is shown in Fig. 2. It consists of a sillimanite tube,[4] T_1, which is cemented with sealing wax into the water-cooled metal head, H. This is closed by a glass cap, C, which is cemented to the head by the sealing wax contained in the annular groove, A. A window is provided in the center of the cap to permit observation and optical temperature measurements. The cap is also provided with a side tube, G, containing an iron slug. The sample, in the form of short lengths of rod, is placed in this side tube from which it can be dropped into the furnace as desired by moving the iron with a magnet. The glass falls into the sillimanite crucible, F, which is deep enough to contain the resulting foam. The furnace is connected to the pumps and the analytical system through the tube, V_1, which connects with the glass in a copper-to-glass seal. To insure a good vacuum the tube, T_1, is surrounded by a second tube, T_2, and the space between is evacuated through V_2 by an oil pump. It was found later, however, that with good refractory tubes this vacuum jacket is unnecessary. The furnace is heated by a platinum resistor wound on an alundum core. A thermocouple is inserted between the furnace core and T_2. The temperature of the outgassing glass, however, is measured by an optical pyrometer through the window at the top of the furnace tube.

The most troublesome source of error in the work has been the reabsorp-

[4] From the Champion Porcelain Co., Detroit, Mich.

tion of the gases by substances that are volatilized from the glass and condense in the cool upper section of the furnace tube. Sodium oxide is probably the worst offender. If a very heavy deposit, such as accumulates from several successive determinations, is formed the gases may be almost completely absorbed. Methods have been found for diminishing this effect, but so far no way has been found to eliminate it. A new crucible is used for each determination and the furnace tube above this is protected by a silica tube which can be removed and cleaned between each determination. Also the extraction of the gases is carried out as rapidly as possible.

The analytical apparatus is sketched in Fig. 3. It is constructed throughout of Pyrex-resistant glass No. 774. It provides a means of measuring the pressure in the furnace, of pumping out the gas as it is liberated, and of analyzing for H_2O, CO_2, SO_2, O_2, H_2, and CO. The apparatus is most easily understood by following the procedure in a typical analysis. A 5- to 10-gram sample of the glass to be analyzed is placed in the sample tube, *G*, of the furnace (Fig. 2). The glass is in the form of pieces of rod about 1 centimeter long and $^1/_2$ centimeter in diameter. The cap is now cemented to the furnace head and the furnace is exhausted and brought up to temperature. The baking out is continued until the pressure reading on the Pirani gage, *E*, indicates that a good vacuum has been obtained. Meanwhile the stopcock, S_1 (Fig. 3), is turned so that 1, 2, and 3 are connected together. This is a special stopcock bored so that by turning to the proper position connections can be made between all three entering tubes or between any two alone. The cup on the upper end of the stopcock contains vacuum pump oil thus eliminating any possibility of a leak from the outside. The pumping-out process usually requires several hours, or longer with new furnace tubes. When the pumping is complete, stopcock S_3 is closed and S_1 is turned so as to connect 1 and 2 and close off 3. The trap, *T*, is then cooled with solid CO_2, and the sample of glass is gradually added to the furnace. As the gases are liberated they pass from the furnace through the trap, *T*, where the water is removed and from there into the bulb, *B*. From here the gas can be pumped into the space between S_1 and S_2 by raising the mercury from the reservoir, R_2, which is sufficient in volume to fill the bulb, *B*, and the tubing as far as S_2. The bulk of the gas is given off in the first few minutes of heating, but there is a gradual evolution which continues for some time. In the experiments carried on by the writer the gases are collected for half an hour after which time the stopcock, S_0, is closed and the mercury in the reservoir, R_1, is raised so as to trap the water in *T*. The solid CO_2 mixture is now removed, and a bath of boiling water brought up so as to immerse the trap and the connecting tubing completely. The mercury is now set at the calibration points, *A*, *A*, for which the enclosed volume has been determined, and the pressure is read on the scale, M_1.

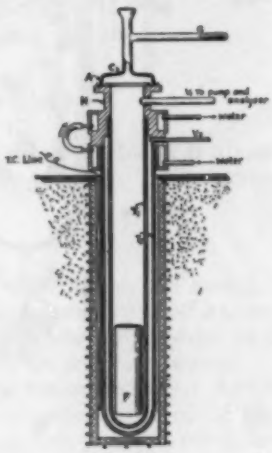

FIG. 2.

In this way the quantity of water is determined. This method may be used for the measurement of very small quantities of water if the volume of T be kept small. The mercury is now lowered, and S_3 is opened to pump out the water. The total quantity of gas other than water is measured by raising the mercury from R_2 to the point, P, opening S_2 until the gas flows into B, closing again, and raising the mercury to one of the calibrated points, V_{0-5}, for which the enclosed volume is known. This value of the volume, together with the pressure reading on M_2, suffices to determine the quantity of gas. This is in error, of course, in the ratio of the volume between S_1 and S_2 to the total volume above P. This, however, is of the order of only 1%.

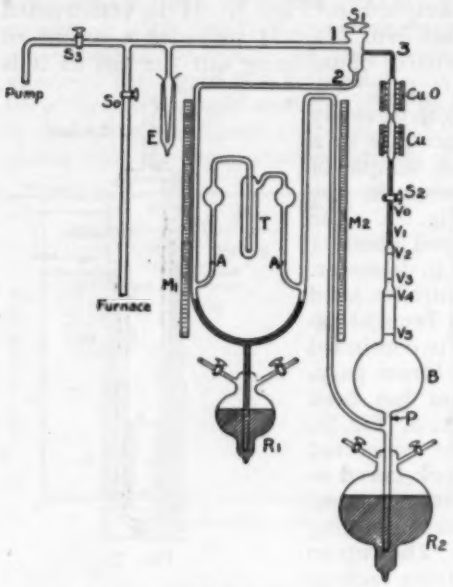

FIG. 3.

The trap, T_1, is now immersed in liquid air, S_1 is turned to connect 2 and 3, and the gas is circulated around several times and finally returned to the space between S_1 and S_2. In this way CO_2 and SO_2 are removed. The amount may be determined either by measuring the quantity frozen out as was done with water or by the decrease in quantity of the remaining gas. If it is desired to remove CO_2 and SO_2 separately, the trap is held at $-130°C$ by a special cooling bath for the separation of SO_2 and then cooled as above for the separation of CO_2. To be sure of the nature of the gas frozen out, the vapor pressure is followed as the trap warms up. The vapor pressure of a gas is a fairly characteristic property and in a case like the present, where, due to the conditions of high temperature under which they are expelled from the glass, only a few gases could occur, it serves as a satisfactory identification.

After being determined, the CO_2 and SO_2 are pumped out as in the case of water. The oxygen is then measured by determining the decrease in amount when the gas is passed over hot copper in the tube marked Cu. Carbon monoxide and H_2 are determined similarly by passing over hot CuO and freezing out the products of oxidation. The fact that the gases come from molten glass excludes the possibility of both oxidizing and reducing gases being present in appreciable proportions so that this part of the analysis is fairly simple. In fact, in practice it is found that whenever there is an appreciable quantity of gas at this point it proves to be oxygen. Reducing gases like CO and H_2 and inert gases like N_2 have never been found in sufficient quantities to be certain of their identity.

A few test analyses and blank runs have been made, although this has

not been carried very far since there are other sources of error which must be eliminated before refinements in the analytical system are justified. Table I gives some examples of test analyses and an example of a blank run. The figures refer to the gas volume at standard conditions. In this blank run everything was carried out as in an actual experiment, except that no glass was added to the crucible. The values are calculated to refer to 100 grams of glass in the same way as the results of a regular analysis.

TABLE I

TEST ANALYSES

No.	Added	Found
1	SO_2 0.71, CO_2 0.76	SO_2 0.71, CO_2 0.75
2	SO_2 0.61, CO_2 0.91	SO_2 0.63, CO_2 0.90
3	Air 2.79	O_2 0.57, N_2 2.22
4	Air 1.82	O_2 0.39, N_2 1.43
5	CO 0.39	CO 0.38
6	H_2O 1.20	H_2O 1.22

Blank on Apparatus

H_2O 0.7 CO_2 0.1 $O_2 + N_2$, etc., 0.1

As will appear later the total volume of gas obtained in the blank is about 2% or less of that obtained from an average sample of glass. This is considered small enough for practical purposes.

III. Results

About 150 analyses have been made with the apparatus. All samples examined except those that had been previously outgassed gave off appreciable quantities of gas, the amount varying from a few hundredths to a few tenths per cent by weight. No attempt will be made, however, to give all the results but only typical examples of the various classes. In all of the results that follow the quantities of gas are expressed in terms of the number of cubic centimeters at 0°C and one atmosphere pressure obtained from 100 grams of glass.

Consider first the results with a simple glass containing only soda, lime, and silica, that is, a glass without fining agents or coloring agents. Glass A in Table II is such a glass. The composition is approximately SiO_2 75%,

TABLE II

Glass No.	H_2O	CO_2	$O_2 + R$	SO_2
A	33	7	2	
B	33	3	47	
C	25	2	13	16

Na_2O 15%, and CaO 10%. A little niter was added to the batch to fix the state of oxidation. The melting was carried out in a 100-pound pot at about 1400°C. The glass contains a good deal of water, a moderate amount of carbon dioxide, and a little oxygen. With the oxygen is included any inert gas as N_2, etc., since it is present only in very small quantity if at all. The total volume of gas is of the order of the volume of the glass itself. This is often the case. There is no difficulty in accounting for the different gases that are found present in this glass. It is not surprising that water should be the principal gas since each of the separate

oxides that go to make up the glass reacts with water; in fact Na_2O and CaO form quite stable compounds with it. The CO_2 comes, no doubt, from undecomposed carbonate. The oxygen is not so readily accounted for but it probably comes from the breakdown of Fe_2O_3 (always present as an impurity) into oxygen and FeO.

The effect of adding arsenic to the above glass can now be seen. Glass B, Table II, is like A but has added to it $^1/_2\%$ As_2O_3 with enough $NaNO_3$ to oxidize it to As_2O_5. The chief difference in the gases is the large increase in oxygen content coming from the decomposition of As_2O_5 into As_2O_3 and O_2. It is this ability to give off oxygen which is probably responsible for the fining action of arsenic. This is in agreement with observations of Turner and others that the arsenic itself is not volatilized and that for good results it must be in the oxidized state. The mechanism of fining by arsenic appears from the present experiments to be as follows: As the batch melts down a number of fine seeds are trapped in the glass. Some of these are so small that they would require indefinitely long periods of time to rise. These fine seeds act as nuclei for the liberation of the excess oxygen from the pentavalent arsenic. This liberation of oxygen increases the size of the bubbles so that they can rise and escape in a reasonable length of time. Experiments with glucose solutions have shown that the presence of an excess of some gas, *e.g.*, NH_3, in the solution does in fact result in a fining action of the type here postulated. These low-tempera-

TABLE III

Glass No.	H_2O	CO_2	$O_2 + R$
A	33	7	2
D	74	1	1

ture experiments have the advantage that the progress of the process can be watched. The explanation suggested here should not be confused with the frequently advanced idea that bubbles from the arsenic in rising through the glass sweep out the other bubbles. In the ideal case according to this picture, the gas from the arsenic forms no bubbles but only increases the size of bubbles already present.

Returning to the gas analysis results, Glass C, Table II, is an example of a glass with about $^3/_4\%$ of salt cake added. In this case sulfur dioxide is obtained in addition to the gases already mentioned. This comes, of course, from the decomposition of the sulfate, oxygen being formed at the same time. The volume of oxygen from this source should theoretically be half that of the SO_2. In the case of the example given it exceeds this due to the presence of a small quantity of arsenic. The remarks made previously in regard to the fining action of arsenic apply also to the case of sulfate.

The results for a simple borosilicate glass are shown in Glass D, Table III. The values for Glass A are repeated for comparison. Like the lime glasses the borosilicates in general contain water, carbon dioxide, and oxygen. The water content, however, is generally higher in the borosilicates. The carbon dioxide content, on the other hand, is in general lower due to the acid nature of B_2O_3.

It was noted early in the work that the size of the original melt had a large influence on the gas content. This is illustrated in Table IV which gives the data for a soda-lime-silica glass melted in various quantities.

The water content of the 100-pound melt, A, is nearly twice that of the 100-gram melt, A″, in spite of the fact that the large melt was heated for a much longer period in melting. This is probably due to the fact that in a small melt made in an electric furnace the air sweeps away the water, carbon dioxide, etc., from the melting batch, whereas in a large melt the majority of the batch melts in an atmosphere of these gases. Further experiments to be published later have shown that the moisture content of glass is a function of the partial pressure of water vapor in the furnace atmosphere during melting. It is therefore quite reasonable that the large melts should have a higher water content since they melt in an atmosphere of higher partial pressure of water vapor. In the case of carbon dioxide, with ordinary glasses the writer has been unable to increase the content in the glass by introducing the gas in the furnace atmosphere so there is no reason to expect the carbon dioxide content to depend on the size of the melt. In other words in the case of water absorption a reversible phenomenon near equilibrium is being dealt with, while with carbon dioxide the small amount usually present in the glass is greater than the equilibrium value and owes its retention to the sluggishness of vitreous systems. This agrees with the work of Weyl[5] on carbon dioxide-containing glasses. Even with relatively basic glass he found it necessary to go to very high

TABLE IV

Glass No.	Melting	H_2O	CO_2	$O_2 + R$
A	24 hr. at 1350°C in 100-lb. pot	33	7	2
A′	16 hr. at 1350°C in 1-lb. clay crucible	25	7	2
A″	6 hr. at 1350°C in 100-gram porcelain crucible	18.4	6	1

pressures to obtain appreciable quantities of carbon dioxide in the glass. His results indicate that an ordinary soda-lime glass should have not over one thousandth of a per cent by weight of carbon dioxide in equilibrium with the gas at one atmosphere and 1400°C. This would amount to less than $^1/_2$ cubic centimeter in 100 grams of glass which is less than we find present. Hence it would not be expected that the partial pressure of CO_2 in the furnace atmosphere would have any effect on the CO_2 content. In the case of water no data were found in the literature that would permit even a rough estimate of the water content of glass that would be in equilibrium with water vapor at one atmosphere and 1400°C.

It is interesting to note that experiments have shown that remelting a glass has little effect on its gas content. The glass in these experiments, however, was not powdered before remelting. This result and others on gas content as a function of the time of melting show that in an undisturbed melt the gases reach their final values quite early in the melting process, and from then on any change is slow.

It should be mentioned that when glasses are evacuated at high temperature there are volatilized, in addition to the gases so far discussed, various substances that are solids at room temperature and that condense in the cold upper sections of the furnace tube. The most common of these are Na_2O and B_2O_3. With arsenic-containing glass As or As_2O_3 may occur. Zinc and lead glasses volatilize ZnO and PbO, respectively, or under sufficiently reducing conditions the corresponding metals. In fact these sub-

[5] W. Weyl, *Glastech. Ber.*, **9**, 641 (1931).

limates obtained from glass are sometimes quite characteristic of a glass and might be helpful in identifying it.

The work is being continued with a refined apparatus. Other types of glasses are being analyzed and measurements are being made on the solubility of gases in glass.

Acknowledgment In conclusion, the author wishes to express his thanks to W. C. Taylor and H. P. Hood for suggesting and supervising the work and to Mr. Jacoby for assistance in carrying out the experiments.

CORNING GLASS WORKS
CORNING, NEW YORK

A PECULIARITY OF SHEET-IRON ACID RESISTING COVER COAT ENAMELS*

By H. E. Ebright and J. E. Hansen

ABSTRACT

It has been demonstrated that the small bare spots evident in the first coat of acid-resisting enamel applied directly upon the ground coat are not necessarily the result of a process fishscaling in the ground coat during the firing operation, but are more often the result of reboiling of the ground-coat enamel and lack of film strength in the yet unfused layer of acid-resisting enamel. Reboiling, or other mechanical movements of the ground coat, may promote defects in acid-resisting enamels which would not be visible in those of the nonacid-resisting type, particularly when these enamels are applied directly upon the ground coat. The electrolytes used with acid-resisting enamels are directly connected with the popping condition noted. A choice of the proper kinds and amounts of electrolytes for "setting-up" the enamel can, in some cases, eliminate or minimize this trouble. The use of a nonacid-resisting enamel, properly set up as an intermediate layer between the ground coat and the finish coat of acid-resisting enamel, will also prevent troubles of this kind. The tendency for this peculiar defect to occur depends also upon the type of enameling base metal used and its tendency to reboil.

I. Introduction

In the early stages of the research and development work on acid-resisting sheet-iron cover-coat enamel, upon examination of the fired first coat of acid-resisting enamel applied directly upon the ground coat on flat sheets, it was noted that a defect occurred which resembled process fishscale, that is, fishscaling which occurred at the time of firing the first acid-resisting cover coat. This same apparent process fishscaling did not take place when using a nonacid-resisting enamel over the same ground coat and same type of base metal.

As it became evident that better opacity, covering power, and wider working range could be obtained by using a first cover coat of nonacid-resisting nature and a finish coat of acid-resisting enamel, this peculiarity was gradually lost sight of, except at such times as workers in other laboratories or in customers' plants observed the same effect and were curious as to why acid-resisting enamels caused the ground coat to process fishscale whereas nonacid-resisting enamels did not.

(1) Forty Seconds at 1500°F In the course of an investigation on the so-called reboiling of sheet-iron ground-coat enamels, samples were prepared by applying a coat of acid-resisting enamel directly upon the previously fired sheet-iron ground coat. These samples were placed upon red hot tools and introduced into the furnace at the cover-coat firing temperature of 1500°F. At the end of 40 seconds the samples were withdrawn from the furnace, cooled, and examined for reboiling. The cover-coat enamel had become sintered but not fused, and reboiling of the ground coat was so aggravated that it actually pushed spots of the sintered or baked cover-coat enamel up above its normal plane, so that the whole surface had a closely pimpled appearance. Approximately 20 to 25 spots per square foot were visible in the cover-coat layer where the bisque had broken away, in much the same type of fracture as would have been the case had the ground-coat enamel fishscaled (see Fig. 1). When the bisque surrounding these spots was scraped off with a knife and the ground coat was examined, no fracture indicative of

* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Enamel Division). Revised copy received April 1, 1933.

fishscale was in evidence, but the center of each one of these spots was occupied by a reboiling blister.

This was direct evidence that the local "spot fractures" in the sintered acid-resisting cover-coat enamel were the result of its actually having been punctured and fractured by the reboiling blisters of the ground coat.

(2) Thirty Seconds at 1500°F Similar samples were prepared and after being placed upon red hot pins were introduced into the furnace at a temperature of 1500°F for a period of approximately 30 seconds. This heat treatment was enough to develop the reboiling blisters in the ground coat as well as a slight film strength in the layer of dry acid-resisting enamel, but not sufficient to result in any bonding between the layer of dry, unfused enamel and the previously fired ground coat. As the samples cooled, the layer of slightly sintered cover coat commenced to loosen around the outside edges of the sample, and it was possible to lift off or remove the layer in a sheet of considerable size. Examination of the underside of this layer showed it to be indented with hundreds, if not thousands, of depressions in the exact counter-pattern of the reboiling blisters on the ground coat from which it had been removed. This layer likewise had been punctured in several spots where particularly large reboiling blisters had progressed to such a degree as to exceed the film strength of the unfused acid-resisting cover-coat enamel and to fracture it (see Fig. 2).

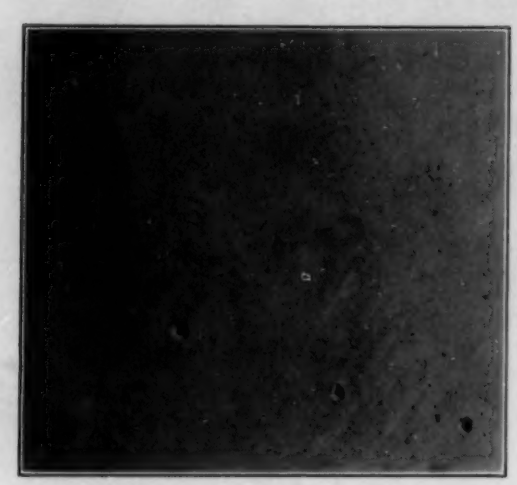

FIG. 1.—Fractures in bisque first cover coat due to reboiling of ground coat.

(3) Nonacid-Resisting 30 Seconds at 1500°F A similar trial was made by applying nonacid-resisting enamel on the same ground-coat mixture on similar base metal and by making the 30-second reboiling test. In this case again, reboiling had progressed to the state that it developed a pimpled surface on the bisque enamel and, while the unfired enamel could be brushed off the underlying ground coat with a stiff bristled brush, the film strength was such that no spalling or flaking occurred at the edges, nor could the layer be detached from the underlying ground coat. No puncturing of the cover coat due to aggravated reboiling was in evidence.

NOTE: The acid-resisting enamel used was one of a highly commercial type in quite general use, and the frit was milled with 7% Vallendar clay, 6% tin oxide, and 0.25% ammonium alum.

The nonacid-resisting cover coat was also of the commercial type milled with 7% Vallendar clay, 6% tin oxide, and 0.125% magnesium carbonate.

(4) Other Mill Additions Check trials were made using other of the common setting-up agents with results as follows: (*1*) *boric-acid mill addition:* entirely free of the "popping" or puncturing of the acid-resisting enamel; (*2*) *potassium-acid sulfate mill addition:* entirely free from "popping"; (*3*) *aluminum-sulfate mill addition:* entirely free from "popping"; (*4*) *sodium-aluminate mill addition:* a bad case of "popping" as the reboiling of the ground coat punctured the cover-coat film in many places; and (*5*) *sodium aluminate-boric acid mill addition:* a mild case of "popping," but not as bad as when sodium aluminate alone was used as the setting-up agent.

The standard nonacid-resisting sheet steel white cover-coat enamel, milled with 7% Vallendar clay, 6% tin oxide, and 0.25% ammonium alum, was applied on the previously fired ground coat and a 30-second

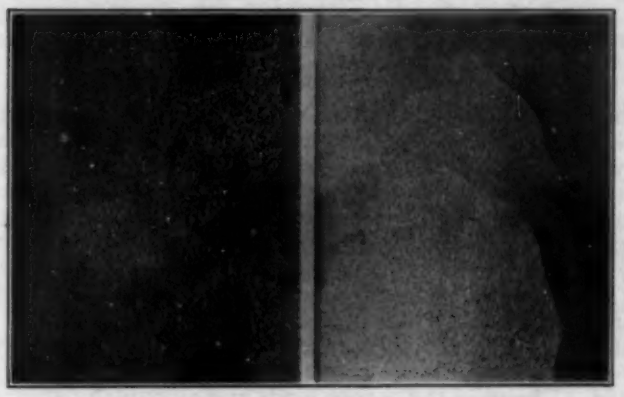

FIG. 2.—Reboiled ground-coat sheet (left) and reverse side of cover-coat film removed from same (right). Note holes in cover-coat film as exact counter pattern of large reboil blisters in ground coat.

reboil test was made at 1500°F. The results were the same as when alum was used as a setting-up agent for the acid-resisting enamel. The reboiling of the ground coat punctured the film of cover-coat enamel in many places causing "poppers," and the dried layer of enamel could be lifted off in a large piece from the underlying ground coat.

It was noted that the original samples with the alum mill addition which showed "poppers" also showed faint "shore lines,"[1] when properly and completely fired. The liquid enamel was then "set-up" with the equivalent of 50 cubic centimeters of concentrated sulfuric acid (specific gravity 1.84) per 100 pounds of frit, and samples were tried. In these trials the "shore lines" were absent and the "poppers" were entirely eliminated.

These data are not offered as a condemnation of ammonium alum or

[1] Shore lines are irregular contours of the surface, usually around the edges, visible in the fired enamel, and probably the result of a local concentration of soluble salts. They are not to be confused with hair lines or craze lines, as the coating is continuous. Shore lines derive their name from the similar contour of an ocean shore where the waves have washed the sand and piled it in ridges.

other alums as setting-up agents for acid-resisting enamels, since they are excellent for the purpose if used in the proper amount or if a small amount of sulfuric acid is used in addition to the alum. Likewise when the acid-resisting enamel is used as a finish coat over a first cover coat of nonacid-resisting enamel, no trouble from "poppers" is encountered.

(5) Different Metals During the collection of these data, commercial steel bases from three manufacturers were used and the same "apparent process fishscaling" or "poppers" were developed to a greater or less extent, depending on the reboiling tendency of the metal.

Samples of the original enamel with the ammonium-alum mill addition were run on ground-coat samples of another steel base of a so-called "non-reboiling metal" and not only was it impossible to produce the "popping" tendency but it was also impossible to cause the layer of dry unfused enamel to separate from the previously fired ground-coat layer when the reboiling test was carried out.

II. Conclusions

It has been demonstrated that the small bare spots evident in the first coat of acid-resisting enamel applied directly upon the ground coat are not necessarily the result of a process-fishscaling in the ground coat during the firing operation, but are more often the result of reboiling of the ground-coat enamel and lack of film strength in the yet unfused layer of acid-resisting enamel. Reboiling, or other mechanical movements of the ground coat, may promote defects in acid-resisting enamels which would not be visible in those of the nonacid-resisting type, particularly when these enamels are applied directly upon the ground coat.

From the experimental results it is evident that the electrolytes used with acid-resisting enamels are directly connected with the popping condition noted. Choice of the proper kinds and amounts of electrolytes for "setting-up" the enamel can, in some cases, eliminate or at least minimize this trouble, as is illustrated by the use of ammonia alum with the addition of a small amount of sulfuric acid.

The use of a nonacid-resisting enamel, properly set up as an intermediate layer between the ground coat and the finish coat of acid-resisting enamel, will also prevent troubles of this kind.

The tendency of this peculiar defect to occur depends also upon the type of enameling base metal used and its tendency to reboil.

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PROGRESS REPORT ON THE STUDY OF GASES IN ENAMELING IRON*

By Ralph W. Baker[1] and J. C. Joublanc[2]

ABSTRACT

Since all ferrous materials contain within their structure a varied assortment and quantity of gases, a discussion is presented of the effect of such factors as time, temperature, atmosphere, and deliberate methods used in the manufacture of enameling iron. A study of the important gaseous impurities in ferrous materials is given. Melting investigations were made to determine at high temperatures the absorptive capacity of specially prepared irons for air, nitrogen, hydrogen, and carbon monoxide, and the influence of carbon, manganese, silicon, and aluminum on the absorptive and retentive capacities. Manganese in increasing amounts increased the absorption of all gases. A critical percentage content of 0.25% of manganese was found to exist, at which maximum absorption of nitrogen occurred; below and above this percentage content the absorption of nitrogen decreased.

Many grades of enameling iron were subjected to a similar investigation. Certain irregularities of various analyses of commercial irons were noted in that there were irregularities of absorption and retention of gases in a range of temperature which included the temperature at which porcelain enamels were fired. The enameling iron of low carbon and low manganese content, containing only the permissibly low phosphorus, sulfur, silicon, and alloying elements, should insure dependable performance during enameling operations.

I. Effect of Time, Temperature, Atmosphere, and Methods Used in the Manufacture of Enameling Iron

All ferrous materials contain within their structure a varied assortment and quantity of gases which depend fundamentally upon conditions of time, temperature, atmosphere, and methods used during the refining operation in the furnace and the cooling period in the ingot mold. The factors, therefore, which control the gas content of a unit quantity of cold metal will be discussed.

Only the ferrous metals which are being increasingly adapted to porcelain enameling were used. The requirements for the base metal have changed recently. Necessary changes in the composition, texture, and properties of the porcelain enamel as well as altered specifications covering the forming actions of the base metal have excluded ordinary steel from the list of satisfactory base metals. High-grade base metal has become a necessity for a satisfactory porcelain enameled product. High-grade base metals are produced like steel in the mill through the refining of raw materials in the basic open-hearth furnace. The higher grade base metals (irons) require a refinement in addition to that needed for steel.

The commercial elements, such as carbon, manganese, phosphorus, sulfur, silicon, and alloys, which are necessary and subject to control in the usual ferrous metals are subject to greater control in the manufacture of high-grade enameling iron. In fact, the interpretation of the word "high grade" partially represents not the absolute freedom of these elements but their presence in small quantities.

In addition to the minute quantity of solid impurities required in enameling iron, a small quantity of gaseous impurities is a justifiable requirement.

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* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Enamel Division).

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There are also the factors of time, temperature, atmosphere, and deliberate methods used which control the gas content of ferrous materials.

(1) Time Insufficient time for the refining period naturally represents insufficient refinement in the furnace, that is, an insufficient decrease of solid and gaseous impurities. An over-sufficient time period permits excessive chemical combination of the molten iron with the oxygen of the atmosphere or with the gas of the fuel.

(2) Temperature Temperature plays essentially the same rôle. A temperature range exists in the open hearth below or above which undesirable chemical and physical changes take place. An exact temperature exists at which each grade of ferrous material must be poured from the furnace to the ladle and into the ingot to prevent excessive chemical absorption or mechanical entanglement of solids and gases.

(3) Atmosphere The atmosphere of an open-hearth furnace is oxidizing. The molten bath is protected by a layer of slag from excessive oxidation, but there are elemental gases from the fuel, from the air within the furnace, and from the water vapor in the air, which become chemically combined and mechanically held in the molten iron.

(4) Control Methods The methods used to minimize solid and gaseous impurities are chemical and physical in nature. The chemical control is represented by skilled open-hearth furnace practice, followed by the introduction at the end of the refining period of gas solvents, that is, elements that combine with and fix the gases, thereby altering the solubility of gases in the base metal. The physical control is represented by the quiescence or stirring of the ladle charge.

II. Study of Gases from the Standpoint of States of Existence and Percentage Content Determinations

The amount and action of gases in enameling iron is an important phase of this subject. It must be remembered that these irons have been subjected to various deliberate methods of refinement. These unavoidable gases which are not seen, but manifest themselves during enameling operations, are oxygen, nitrogen, hydrogen, and carbon monoxide. Gases, singly or collectively, are contained in iron and steel in three states, (1) dissolved or combined, (2) mechanically trapped or occluded, and (3) reactionary, or formed, as the result of reaction within the material.

As the temperature of iron or steel is raised, its ability to dissolve, occlude, or form gases through reaction is increased. Likewise, as the iron or steel cools from the elevated temperatures to room temperature, the same chemical and physical principles which caused absorption during increasing temperatures now cause evolution or discharge of part of the gases during decreasing temperatures.

Oxygen, for instance, is essentially dissolved or combined in the form of iron and manganese oxides. Total oxygen is determined by the vacuum-fusion method in which, through melting of the sample in a graphite crucible in vacuum, measurements can be made of the volume of the oxygen, reduced by carbon from nonmetallic oxides through absorption of the resulting carbon monoxide.

Nitrogen, likewise, is usually found in the dissolved or combined state

in the form of nitrides. The analysis for percentage content involves the solution-distillation method, the conversion of nitrogen to ammonium hydroxide, volumetrically determined. The vacuum-fusion method recovers even more nitrogen, particularly that trace held uncombined.

Part of the hydrogen is in the combined state in the form of the hydride, but generally a portion is mechanically trapped by absorption or occlusion. Hydrogen is expelled from the sample by vacuum melting, converted to moisture or water, and gravimetrically determined.

Carbon monoxide occurs in all of the accepted states. Iron and manganese have a solvent power for carbon monoxide with the formation of iron and manganese carbonyls. This gas takes other forms of combination. Carbon monoxide is actively absorbed and thus mechanically held. A portion of gas is considered as reactionary or the result of the chemical reaction of iron oxide and carbon, evolving carbon monoxide which is dissolved or trapped. This carbon monoxide expelled from the metal chemically or by heating is absorbed in the form of carbon dioxide and is thus gravimetrically determined.

III. Melting Experiments to Determine at High Temperatures the Absorptive Capacity of Specially Prepared Steels for Air, Nitrogen, Hydrogen, and Carbon Monoxide

It was not the intention of the authors to measure empirically the state of existence or content of gases in the samples, but rather to measure the fluctuation of gas volume in a closed system. This fluctuation is a measure of the relative absorption or evolution of the gases by the sample. The measurement therefore becomes relative and not empirical. These relative measurements were made by using a standard for comparison. In the present tests, helium gas was used because helium exhibits only a slight tendency to dissolve in or combine with ferrous materials. The procedure was (1) to clean the air from the system, (2) to arrive at and maintain atmospheric pressure, (3) to close the system in the presence of helium, and (4) to apply heat.

One of the principal sources of error is the evolution of gases from furnace walls and hot refractories. A high ratio of metal sample surface to preheated refractory surface was maintained to correct this error.

During the temperature range from 1600°F to the melting point, volume measurements were taken, after which the gas expansion was plotted against the temperature to obtain a blank curve (theoretical expansion curve), that is, a curve which all gases would follow in the absence of material which dissolves them. If a sample of iron and steel were introduced and the measurements were repeated with any gas, the new expansion curve would not coincide with the blank curve. It follows then that any lowering of the expansion curve during the heating of a specimen must be due to absorption of gas into the sample at a specific temperature.

The relative evolution and retention of gases by iron and steel during decreasing temperatures can be studied in the same manner as the relative absorption of gases during increasing temperatures. Therefore, by varying the chemical analysis of the iron or steel, the individual or collective effect of carbon, manganese, silicon, and aluminum on the ability of iron or steel to absorb gases during increasing temperatures and to retain gases during decreasing temperatures may be tested.

With specially prepared steels it is of interest to study the tendency of the carbon of the steel to decrease the absorption of carbon monoxide by the steel. The higher the carbon content, all other things being equal, the lower will be the solubility of carbon monoxide gas. The actual curve for the high carbon steel, however, exhibited an irregularity during heating and cooling; the curve was not smooth, but fluctuating, and therefore promised a tendency of the high carbon steels to be undependable.

The low carbon steels tended to decrease the solubility and the retention of air and nitrogen and had no appreciable effect on hydrogen. There was, however, a characteristic smoothness to the absorption and retention curves of the low carbon steels for these gases.

Manganese, in increasing amounts, increased the absorption of all gases but carbon monoxide. There existed for all gases but carbon monoxide and particularly for nitrogen a critical percentage content of 0.25% manganese, at which the maximum absorption occurred; below and above this percentage content the absorption decreased. The retention at room temperature of carbon monoxide and hydrogen was increased as the manganese content was decreased. This statement is of value in that one can be assured that there will not be the undesirable great evolution of gas during the cooling of a porcelain enameled low manganese material. Again in the medium and low manganese materials, the gas activity curves were relatively smooth, thus insuring an element of dependability.

The influence of increasing amounts of silicon and aluminum was not particularly noteworthy, except in the case of nitrogen which was absorbed in increasing amounts as the silicon and particularly the aluminum were increased.

A similar investigation was made with carbon monoxide, nitrogen, and hydrogen on five specially prepared heats of enameling iron, all practically identical as to their low carbon, sulfur, phosphorus, and silicon contents. Predicated upon the effect of varying manganese contents on both the gas activity and enameling characteristics, the manganese was varied in these heats so that the individual effect of 0.01, 0.06, 0.10, 0.15, and 0.42% manganese, respectively, could be studied.

Manganese in increasing amounts was found to increase the absorption of all gases but carbon monoxide approximately to 2400°F. Above this temperature, conditions were found to be completely reversed.

During temperatures decreasing from the melting point to 1600°F, all five heats retained most of the absorbed gases to a remarkable degree. At room temperature, however, the following distinctions were found: The iron with 0.01% manganese retained twice as much carbon monoxide as the 0.10 and five times as much as the 0.42 manganese iron. The iron with 0.01% manganese furthermore retained $1^1/_2$ times as much hydrogen as the 0.10 and four times as much as the 0.42 manganese iron. The variation in manganese content had little effect upon the relatively small quantities of nitrogen retained. These investigations were made on sheet materials such as would be almost immediately ready for porcelain enameling. Upon the greater retention and therefore the lesser evolution of gas from these low and medium manganese sheets, an interesting and useful interpretation may be drawn.

A similar investigation on many varied analyses of enameling irons has been started but is not complete at the present time. These samples,

which comprised a cross-section of the accepted enameling irons of today, varied in carbon content from 0.01 to 0.04% and in manganese from 0.02 to 0.21%. The sulfur, phosphorus, and silicon contents were markedly uniform.

These samples of enameling irons were transferred in sheet form from the enameling plants to the laboratory. Vacuum fusion determinations revealed the respective quantities of contained hydrogen, oxygen, and nitrogen gases.

The narrow range of the carbon content (0.01 to 0.04%) did not permit interpretation as to the effect of this element on the absorption and retention of gases by the molten iron in the furnace and ingot stages. Nor at this point could the manganese content be correlated with hydrogen content, and only a slight correlation could be made between manganese and nitrogen contents. An increase, however, in manganese markedly lowered the oxygen. One of the 0.03% manganese irons carried almost 0.1% oxygen, whereas the 0.21% manganese iron carried slightly more than 0.01% oxygen.

The answer is that if the refinement of the manganese of the iron were continued in the open-hearth furnace beyond a certain difficult limit, the excess oxygen would enter and become fairly rigidly fixed in the bath and would be difficult to remove. The solubility work, when completed, will clarify these preliminary correlations.

IV. Conclusions

The results of certain carefully conducted investigations have been interpreted in order that manufacturers of high-grade enameling iron may contribute certain concepts that are already fundamental. The materials employed in these tests will have further tests made on them and will be porcelain enameled to reveal the influences on the delicate chemistry of such enameled sheets.

The tests thus far show that the enameling iron of low carbon and low manganese content, containing only the permissibly low phosphorus, sulfur, silicon, and alloying elements, should insure an element of dependability during enameling operations.

Acknowledgment The authors wish to acknowledge the use of the electrically fused crucibles supplied for the tests by the Massillon Refractories Company.

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A SUMMARY OF THE OBSERVATIONS AND FACTS CONCERNING THE PHENOMENON OF REBOILING*

By James Osborn Lord

ABSTRACT

The recent observations and generally accepted facts concerning the phenomenon of reboiling of enamels on sheet metals are listed concisely. Six photomicrographs are presented to show the outstanding characteristics of the enamels obtained by some of the treatments described in the paper. With no attempt at a final explanation, a series of the most obvious deductions to be drawn from the observations of the first portion of the paper is made. In conclusion, some of the various theories that have been expressed to explain reboiling are mentioned and discussed.

I. Introduction

During the past year a tremendous amount of data has been collected in regard to the subject of reboiling of enamels on steel. Great care, keenness of observation, and ingenuity have been used and the facts observed, although often apparently illogical and contradictory, are irrefutable.

Several suggestions have been offered in explanation of the data, and while they can be made to fit the facts if accompanied with a sufficient number of unproved suppositions and modifications, yet search is still being made for a simple, satisfactory answer to the problem.

With full realization that such answers are not always to be had and in no way discounting some of the important theories that have been offered, which may embody the fundamental principles involved in the final answer, it would seem that a clear recount of the principal facts observed and the most obvious deductions to be derived from them might illuminate the way to further effort.

II. Observations

The following observations have been made and checked by competent observers:

(1) Reboiling takes place only on cobalt (and possibly nickel) ground coats, and only on sheet steel.[1]

(2) Reboiling commences suddenly, as the piece reaches a dull red heat, lasts for a few seconds, and then subsides and will not occur again until the piece has been cooled nearly to room temperature.[2]

Note: Hayes, Canfield, and McGohan note that "metal which reboils when enameled in the usual manner does not reboil if not allowed to cool below 500°F."

(3) Electrolytic, vacuum-distilled iron reboils very slightly for one or two heatings only.[3]

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* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Enamel Division). Received May 18, 1933.

[1] Series of papers on "Mechanics of Enamel Adherence" as follows: J. O. Lord and W. C. Rueckel, I, *Jour. Amer. Ceram. Soc.*, **14** [10], 777–81 (1931); W. C. Rueckel and R. M. King, II, *ibid.*, pp. 782–88; W. K. Carter and R. M. King, III, *ibid.*, pp. 788–94; A. McK. Greaves-Walker and R. M. King, IV, *ibid.*, **15** [9], 476–80 (1932); G. H. Spencer-Strong and R. M. King, V, *ibid.*, pp. 480–83; K. Schwartzwalder and R. M. King, VI, *ibid.*, pp. 483–86; G. H. Spencer-Strong, J. O. Lord, and R. M. King, VII, *ibid.*, pp. 486–90.

[2] Anson Hayes, J. J. Canfield, and G. W. McGohan, "Reply to Schaal and Fuller," *Jour. Amer. Ceram. Soc.*, **15** [6], 351–53 (1932).

[3] R. M. King, "Mechanics of Enamel Adherence, VIII," *ibid.*, **16** [5], 232–38 (1933).

(4) Enamels may possibly reboil on copper, but only very slightly.[1]

(5) Experiments recently conducted in the laboratories at Ohio State University fail to show any reboiling in enamels applied to platinum and gold.

(6) If the piece be (*a*) dipped, and one side brushed off, reboiling will not occur; (*b*) sprayed on one side only, reboiling will occur; (*c*) sprayed on both sides and one side brushed, reboiling will occur; (*d*) sprayed on both sides and one side brushed and then sponged clean, reboiling will not occur.[4] In general, pieces enameled or coated in any manner on both

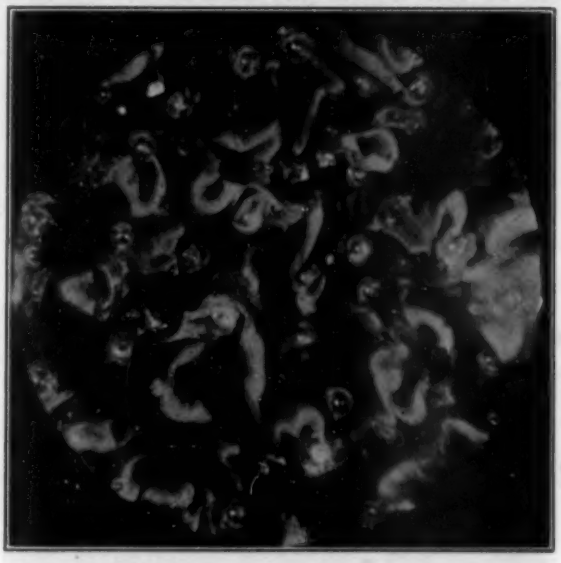

FIG. 1.—Commercial ground coat applied on Armco ingot iron by dipping (laboratory specimen reheated 25 times). (Magnification 45×.)

sides show greater tendency to reboil than when enameled on one side only. A complete description of this behavior is, however, very involved.[2,5]

(7) Sandblasting the surface of the sheet seems to increase the reboiling tendency, particularly if only one side is sandblasted, whereupon that side will reboil.[4]

(8) If the piece is fired *in vacuo*, it will not reboil in any subsequent firing.[3]

(9) As much as 10% carbon dioxide has been found in the gases produced when reboiling takes place.[6]

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[4] Personal communication by W. H. Pfeiffer and H. W. Alexander to R. M. King, February 6, 1933.

[5] Anson Hayes, J. J. Canfield, and G. W. McGohan, "Mechanism of Black Speck Formation in Enamel Resulting from Reboiling of the Ground Coat," *Jour. Amer. Ceram. Soc.*, 15 [6], 338–44 (1932).

[6] A. I. Andrews, An Oral Discussion of Papers on Reboiling at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933.

(10) After twenty-three to twenty-five heatings, no further reboiling takes place.[3]

(11) When, after initial firing, the piece is cooled in the furnace, reboiling will not occur on the next heating. Furthermore, slow heating reduces or eliminates the reboiling tendency.[5]

(12) Pieces reboil more if allowed to rest for several days or longer after the original heating.[4]

(13) Simple glass enamels, without cobalt or nickel, do not reboil.[1]

(14) Some steels reboil more than others.[7]

(15) So far no serious reboiling tendency has been found where

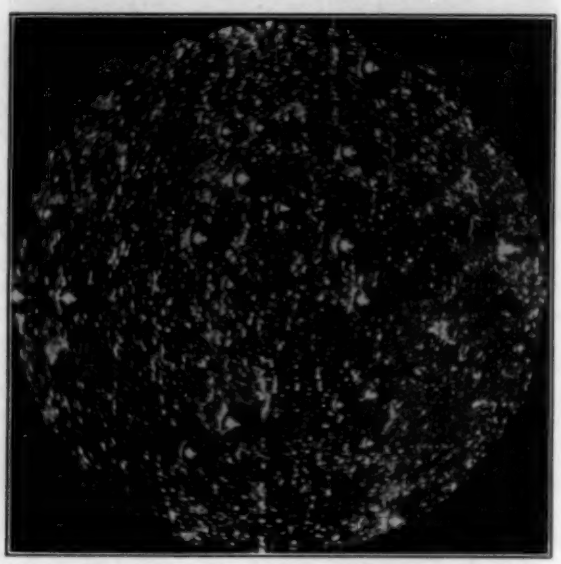

FIG. 2.—Commercial ground coat on copper, reheated 25 times. (Magnification 45×.)

there is no evidence of the metal dendrites observed by Schwartzwalder and others.

III. Microscopic Appearances

Before deductions are drawn from these observations it will be well to present a short microscopic study of some of the surface conditions on ground coats produced in various ways. The photomicrographs (Figs. 1 to 6), taken at 45 diameters, were made very simply by focusing the microscope on the ground-coat surface. Illumination was effected by means of an intense light directed at about 45° to the surface.

For purposes of discussion, somewhat arbitrary but self-evident names for the various kinds of structural features will be selected.

(1) Bubbles These are evident in nearly all of the photomicrographs, varying in size from barely visible to about one-quarter

[7] R. B. Schaal and D. H. Fuller, "Modern Enameling Troubles," *Ceram. Ind.*, **15** [6], 605–14 (1930).

inch in diameter in the original photomicrograph and varying in number from a scattered few to enough to produce practically a foam that obscures the metal entirely.

(2) Clouds and Cloudiness The ill-defined features, some scattered and fleecy, some stringy, and some like a heavy crumpled blanket, are buried in the glassy enamel. A characteristic not observable in these micrographs is the yellow ocher color of the clouds.

(3) Milkiness This is a pale whitish haze that seems to be partly dependent on the thickness of the enamel, sometimes forming an outer zone or band around cloudy areas.

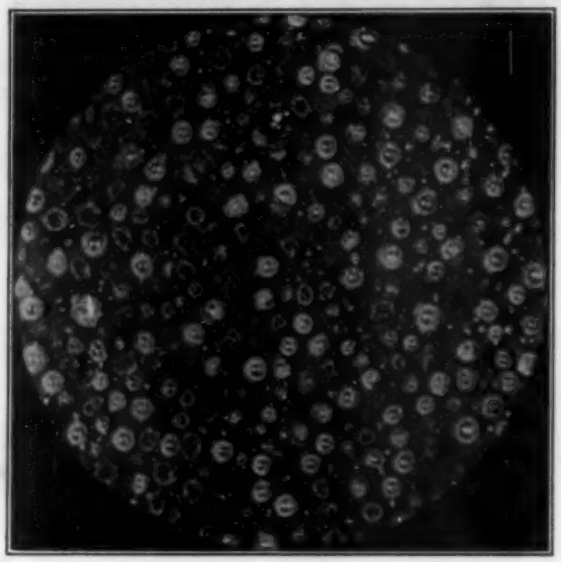

FIG. 3.—Commercial ground coat on Armco ingot iron. correctly fired in air. (Magnification 45×.)

(4) Red Spots These always have a flare of heavy clouds around them as shown in Fig. 5. They are undoubtedly holes in the enamel extending to the metal surface, and are the answer to the question "what are copperheads?" They may be produced by the bursting of very large bubbles, mechanical injury, or imperfect application which allows oxidation or rusting of the metal no longer protected by the enamel.[7]

The vacuum-fired pieces (Fig. 4) show varying degrees of milkiness, but very small stringy or fleecy clouds. The bubbles are very few and small.

In the air-fired pieces, cloudiness seems to be increased by higher temperature of firing and by repeated firings.

Bubbles are clear and small in underfired pieces. As the temperature of firing is increased they become larger and seem to become coated with cloudy material. In some cases the bubble seems to have disappeared, leaving the cloudy envelope looking like a collapsed bag (Figs. 1, 3, and 5).

Numerous examinations indicated that this effect was increased by the number of refirings, and that after twenty-four or twenty-five times very few bubbles were left, but the cloudiness was general and very yellowish in color.

It is interesting to note that white base enamels (Fig. 6), which do not reboil at all, consist of practically a foam of large bubbles. Furthermore, such coatings have very poor adherence.

The enamel on copper (Fig. 2) appears very clear and with a few large

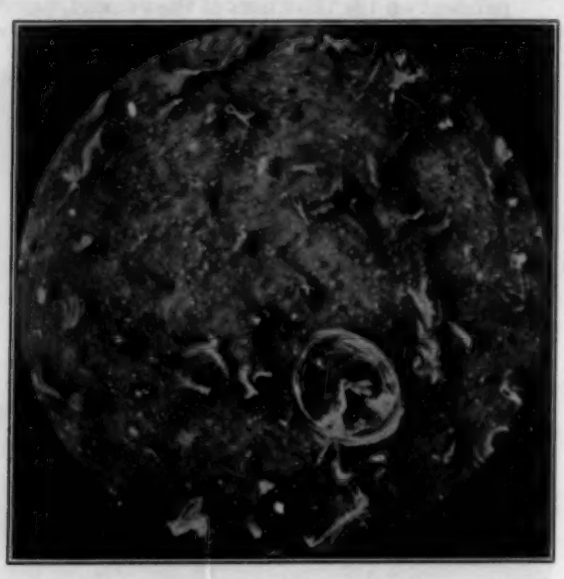

FIG. 4.—Commercial ground coat on electrolytic iron, fired *in vacuo*. (Magnification 45×.)

clean bubbles. Other specimens showed some bright green cloudy areas around some of the bubbles.

IV. Obvious Deductions

Continuing the scheme outlined at the beginning of this paper, the most obvious and uncontrovertible deductions that can be made from the foregoing statements are listed in the same order in which they were made.

(1) To account for reboiling, iron is a necessary factor and also cobalt oxide or nickel oxide.

(2) Some thing or condition is produced to a limited extent on (*a*) cooling from the firing temperature, or (*b*) reheating to the reboiling temperature. This effect is completely consumed by the reboil, and cooling must be repeated to condition the metal for the next reboil.

(3) At least some of the material responsible for the reboil comes from the metal phase. The only possible things are iron oxide, some oxide of carbon, or some dissolved gas such as nitrogen or hydrogen.[8]

[8] R. W. Baker and J. C. Joublanc, "Progress Report on the Study of Gases in Enameling Iron." See this issue, p. 437.

(4) and (5) This is further evidence that the element iron is a factor.

(6) Several suggestions have been offered to explain the erratic behavior of enamels applied in various manners and the effect of the back side coating. (*a*) The coating changes the conductivity and rate of heating through the metal side. (*b*) The coating affects the expansion by warping and hence the state of pressure or strain at the enamel-metal interface. (*c*) Some constituent or compound formed on the coated side passes through the metal and gets into the enamel.

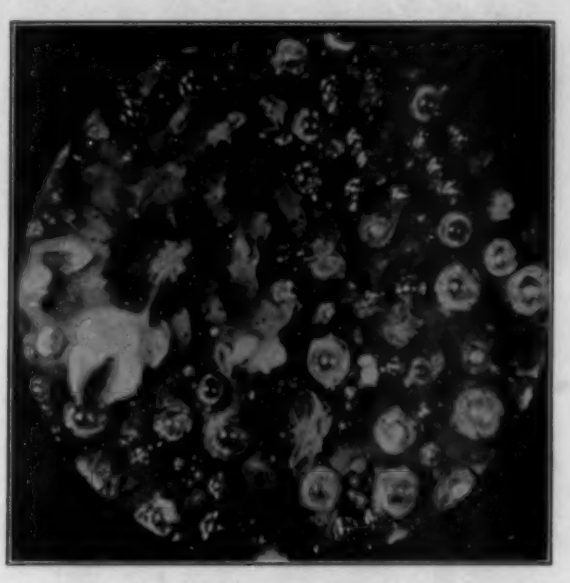

FIG. 5.—Commercial ground coat on Armco ingot iron, reheated ten times. (Magnification 45×.)

At first thought this seems unlikely, although recent experiments have shown that materials such as oxygen (or iron oxide) can penetrate steel to a depth of an inch per hour,[9] and hydrogen at a much faster rate. Even so, it is difficult to see what effect a coating would have in promoting this diffusion and such a theory does not explain the anomalous effects of the various treatments (spraying, brushing, etc.).

(7) It is difficult to see how sandblasting can produce any effect that can be correlated to reboiling, except straining of the surface of the metal.

(8) Whatever reaction is responsible for reboiling, it is sensitive to pressure, and at very low pressures all material available for reboiling is liberated on first heating.

(9) Any general explanation of reboiling must take the nature of the gas into account, and the only sources of CO_2 are from the steel or the carbon in the steel, and carbonates in the enamel.

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[9] (*a*) N. A. Ziegler, "Solubility of Oxygen in Solid Iron," *Trans. A.S.S.T.*, pp. 73–84 (July, 1932); (*b*) Personal communication by Earl C. Smith of the Republic Steel Corporation.

(10) Reheating 23 to 25 times accomplishes what is accomplished in one heating *in vacuo*.

(11) Slow cooling or heating allows reactions, which are only partly completed on quick cooling or heating, to complete themselves. It also minimizes cracking, physical strains, and the like.

(12) Almost any of the suggested explanations can be juggled to explain the effect of a period of rest in promoting reboiling.

(13) Attempts to connect the specific coefficients of expansion of cobalt- or nickel-bearing enamels with the behavior of the enamels have not been

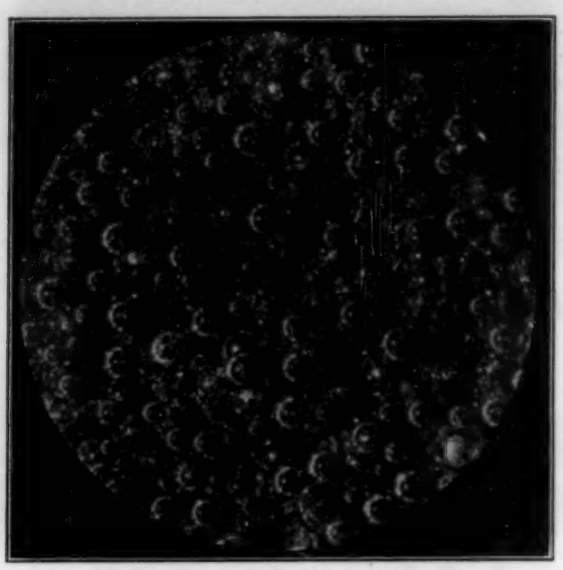

FIG. 6.—White base on Armco ingot iron, fired in air. (Magnification 45×.)

highly fruitful. The chemistry of these substances, on the other hand, has some interesting features.

(14) Eliminating widely variant alloy steels from the discussion, minor variations in composition, impurities near the surface, or physical condition of the surface must be examined to explain why some steels reboil more than others.

(15) It is possible that explanations of adherence, reboiling, dendrites, and cloudiness will be found to be the same.

V. Suggested Explanations

Some interesting theories have been offered to explain and correlate the above ideas and statements, and while each theory is supported with experimental evidence, it is believed that the application of any one theory to all of the observed facts draws a little too heavily on the imagination and requires too many special suppositions and modifications.

The theories that have been suggested are as follows:

(1) The "crack theory" of Hayes, Canfield, and McGohan,[5] in which is

postulated the formation of cracks which connect the already-existing bubbles in the enamel and also allow air from the atmosphere to get into these bubbles. This theory works admirably to explain the cyclic nature of the reboiling phenomenon. It can be adapted to fit many of the peculiarities of behavior of various enamels and under various conditions of application, such as coating one side or both sides if accompanied by some assumptions regarding expansion, state of strain in the enamel surface, etc.

Serious objections to this theory are offered in connection with the volume of gas observed in reboiling, since this is found to be much greater than can be accounted for by entrapped air or coalescence of already-existing bubbles (Schaal and Fuller).[10] Furthermore, it is difficult to see how such a theory can explain the variations in reboiling with different steels, and why reboiling will not take place after twenty-five firings.

(2) The theory that the gas of the reboil comes from the metal also has able support (Baker and Joublanc[8]). The CO_2 found by Andrews[6] in the gases produced by the reboil would certainly indicate this theory to be partly correct at least, since one source of carbon is the steel. Baker and Joublanc point out that steels containing 0.25% manganese are critical in regard to absorption of gases, absorbing the maximum amount of most gases and the minimum amount of CO and hydrogen over steels of other than 0.25% manganese content. The behavior of hydrogen and metals is vagarious on many counts and need not be considered here. In regard to the CO, it is suspected that with manganese contents lower than this the oxide content of the metal can increase in the presence of the small amount of carbon present, allowing the generation of CO to proceed slowly and incompletely. This gives the effect of larger amounts of CO. Above 0.25% manganese, the free oxide present does not give a solubility product high enough to expel any CO gas. Hence, the apparent CO content will be low.

Of course the theory of gas evolution from the metal does not explain the cyclic character of the reboil or the necessity for cobalt or nickel oxides in the enamel.

(3) A theory based on chemical reactions which may be going on at the enamel-metal interface holds forth many possibilities. The present state of knowledge of these reactions, however, makes such a theory purely speculative, but the field is attractive. Consider, for instance, some of the reactions that might take place between the various oxides of iron and cobalt and the metals themselves. The fact should be kept in mind that the surface of the enamel is subject to the oxidizing conditions of the atmosphere, while the portion in contact with the steel is subject to reducing conditions. Diffusion and convection through the enamel layer will tend to prevent either region from reaching a condition of stability. A knowledge of the free energy relationships in the various oxides that might form would give a reasonably good understanding of the oxides which form at any temperature. These free energy relations are not known, but the heat of formation of the various oxides at room temperature is evident. Roughly, the heat of formation per gram atomic weight of oxygen in the compound is proportional to the free energy for that compound at room temperature.

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[10] R. B. Schaal and D. H. Fuller, "Discussion on Reboiling," *Jour. Amer. Ceram. Soc.*, **15** [6], 344–51 (1932).

Generally speaking, those compounds are stable that have the greatest free energy and the greatest heat of formation per gram atomic weight of oxygen.

The following data are obtained from the International Critical Tables:

Compound	Heat of Formation (gram-calories) (per gram molecular weight of compound)	(per gram atomic weight of oxygen)
FeO	67,500	67,500
Fe_2O_3	197,100	65,700
CoO	59,730	59,730
Co_2O_3	142,430	47,477
Co_3O_4 (calculated)	202,160	50,532

The two oxides of iron are very close together and might easily change from one to the other according to such reactions as follow:

			Heat of reaction (cal.)	
	$Fe_2O_3 + Fe = 3FeO$			
Heat	197,100	202,500	+ 5400	(I)
or	$2FeO + O = Fe_2O_3$			
	135,000	197,100	+ 62,100	(II)
	$Co_2O_3 + Fe = 2CoO + FeO$			
	142,430	119,460 + 67,500	+ 44,530	(III)
and	$2CoO + O = Co_2O_3$			
	119,460	142,426	+ 22,966	(IV)

Reactions I and IV have such low heat effects that they might easily be reversed with change in temperature. Reactions I and III show how the iron base might be dissolved by the higher oxides. Note that a reversal of reactions I and III would result in a precipitation of metallic iron (*vid.* Schwartzwalder's dendrites).

Finally, as a rather weak conclusion to this speculation, it might be expected that a change in the nature of these oxides would change the solubility of such gases as nitrogen, CO, and CO_2 in the enamel, thus liberating the gas for reboiling at one temperature and dissolving it at another. This can scarcely be called a theory. It is more a suggestion and a plea for further study of the chemistry of ground-coat behavior.

(4) The suggestion that absorption or condensation of water vapor into cracks is responsible for reboiling has been partly disproved by Andrews.[6] He has found that samples which were cooled in a desiccator after initial firing reboiled on later firing as much as those cooled in air.

(5) If the gases that produce reboiling come out of solution in the enamel phase, anything that will localize the evolution of the gas and cause relatively few large bubbles instead of many small ones, will intensify the damage caused by reboiling. This idea, which may be called the localization theory, leads to some pertinent results. Under certain conditions, a complete absence of localizing points may result in extreme localization of bubbles by the same kind of phenomenon that causes liquids boiled in glass beakers to bump violently: a kind of supersaturation of the gas or vapor in the liquid. On the other hand, a controlled localization in which many small points are provided to start evolution of the gas may overcome the "bumping" effect and give a desirable fine bubble structure.

Many devices may be used to produce such effects. Straining the metal, roughly etching the metal (but not too rough), cracks and checks, strain gradients and composition gradients in the enamel or metal, or fine precipitates in the enamel. In any case, the device may give diametrically opposite effects. For instance, if the metal be strained considerably it might lead to fine bubbles; if not strained enough the localization would be coarser and damaging. A few cracks might be very bad, but a severely checked surface might exhibit a very slight reboil. Again, when the distribution becomes too fine it may revert to the bumping condition and be worse than ever.

Such a theory would explain much of the anomalous behavior of the enamels in reboiling. It is ideal for the speculator because it can be juggled to fit any case.

(6) A theory has been suggested that is based on the idea of changing viscosity in the enamel as the reboil temperature is reached. As the viscosity is lowered fine bubbles combine with each other forming larger bubbles which eventually come out at the surface. In this form, such a theory is open to the same objections as the crack theory, namely, that the volume of gas is not sufficient. If, however, it is considered that reduced viscosity may allow reactions to proceed which are completely blocked at lower temperatures and if, as the temperature increases, gases which may be the product or result of the reactions are concentrated in large enough bubbles to cause reboiling, such a picture fits the facts surprisingly well. This depends, however, on the validity of the chemical theory, as yet unproved.

VI. Conclusions

This paper is intended as a summary of the work that has been done to date by various investigators on the subject of reboiling. No conclusions are drawn as the problem has not yet been solved. The observations mentioned are those that seem most pertinent and most satisfactorily proved. Many items have been omitted because of lack of space and because it was felt they did not contribute especially to the problem. Undoubtedly some interesting points have been omitted unintentionally, but it is hoped that this summary will clear the atmosphere a little and suggest the most profitable paths to pursue in further research.

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EFFECT OF ORGANIC GRINDING MEDIA ON WATER-SOLUBLE SILICA FRITS*

By Helen Blair Barlett and Karl Schwartzwalder

ABSTRACT

The tendency of fine particles of a slightly water-soluble silicate to agglomerate, thus preventing effective determination of grain-size distribution in the dried material, may be overcome by using organic liquids as the grinding media. An explanation is offered for the action of various liquids.

I. Introduction

It is often desirable to determine the grain-size distribution in ceramic materials after they have been wet-ground and dried. This is done readily enough when the powder is insoluble, but if it is even slightly water-soluble the material will have caked so hard in drying that it will be impossible to break the particles down into their original sizes. The finest grains will be the most affected on account of their greater solubility, and will have agglomerated to such an extent that what was originally the most finely subdivided element may now well be the coarsest. Since no satisfactory method of breaking up these agglomerates was found, another way of dealing with the problem has been developed: that of eliminating the effect of water solubility by grinding in an organic liquid.

Information regarding the action of organic liquids on partially soluble, finely ground silicates was lacking. A few liquids in which the frits might not be soluble were tried, namely, (1) ethyl alcohol, (2) butyl alcohol, (3) amyl alcohol, (4) benzene, and (5) xylene. For comparative purposes an insoluble artificial mullite was ground in the same liquids.

The frit was crushed through a 20-mesh screen, and ground with various percentages of liquid. It was found that if 1000 grams of the material were ground with 1000 cubic centimeters of the liquid in one-gallon ball mills the best results could be obtained for comparative purposes. The batches were examined and compared as they were taken from the mills and also after they were dried.

II. Discussion and Results

The action of an organic liquid when used in this manner seems to depend upon whether it is a polar or a nonpolar compound, of which alcohol and benzene, respectively, are representatives. The nature of the solid material is also an important factor, as shown by the difference in behavior of the artificial mullite and of the frit. The phenomena observed are largely explained by a consideration of surface reactions between the silicate particles and the suspending vehicle.

With regard to the rapid settling of the frit in water and the caking at the bottom of the vessel, the explanation is found in the altered character of the surface of each particle due to hydrolysis and leaching out of the alkali, leaving a soft, bulky layer of gelatinous silica around each grain. The cohesion solid-solid then is very high and the adhesion tension solid-liquid very low. When two particles come into contact they cohere strongly. Because the adhesion solid-liquid is comparatively low the particles tend to agglomerate more and more and to coalesce in their outer

* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (White Wares Division). Received May 13, 1933.

margins until most of the water has been expressed, leaving a dense, almost dry cake in the bottom of the vessel despite the abundance of supernatant liquid. Once the frit has been allowed to dry it is not possible to break up the cohering particles, so complete has been the coalescence.

When artificial mullite was substituted for the frit the effect was altogether different. The adhesion tension mullite-water was great enough to prevent flocculation. There was no tendency for the particles to cohere, so they settled slowly and in accordance with Stokes' law. The addition of a small percentage of sodium silicate (water-glass) to the suspension, however, brought about a marked change. The mullite now settled rapidly and formed a dense cake on the bottom of the vessel. It appears that the silicate had been adsorbed at the surface of the mullite particles, causing them to behave in the same manner as the cohering frit particles. This confirms the theory regarding the nature of the surface of the frit. That the hydroxyl ion is not the effective agent in water mixtures was shown by the addition of NaOH to the mullite-water suspension, for no change in the character of the mixture was noted. NH_4OH was also ineffective in producing any change. As would be expected then, the addition of HCl to the frit-water slip did not noticeably affect the character of the slip.

The situation was altered, however, when alcohol was used as the suspending medium. The frit gave a very thick, well-suspended slip, while the mullite-alcohol mixture was characteristically thin. When dried out, both the frit and the mullite were very loosely compacted and could be readily broken down into their original grain sizes. The grinding action was good, probably very close to that obtained with water.

To discover the cause for the difference in behavior of the two silicates the mullite grains were given a coating of sodium silicate as before. On account of the strong dehydrating action of the alcohol on the water-glass it was impossible to introduce it directly into the mullite-alcohol slip. By mixing the sodium silicate with a mullite-water slip, however, and subsequently drying it before adding the alcohol, it was possible to study the character of a mullite-alcohol slip when the mullite had an adsorbed surface layer of partially soluble gelatinous silicate. As in the case of the partially soluble frit, the slip obtained was quite thick and showed little tendency to settle. But the change in behavior was apparently not due to the change in surface characteristics, but rather to the free alkali derived from the soluble silicate. This was shown by the fact that the addition of NaOH to a mullite-alcohol mixture caused it to become quite thick and to behave essentially as the frit slip.

It was still further established that the alkali accounts for the difference in behavior of insoluble and partially soluble silicates in alcohol by adding HCl to the alcohol mixtures. In the case of the partially soluble silicate, the slip became thin, as it is with the insoluble mullite, and showed a tendency to settle out more rapidly. The same effect was obtained when acid was added to the mullite-alcohol slip in which the mullite was coated with sodium silicate. A very slight thinning of the slip was the only apparent effect of the acid when used in connection with an insoluble silicate.

Just what the nature of the reaction is that causes a silicate-alcohol suspension to become thick in the presence of an alkali is not as yet clear. Contrary to the condition in water suspensions, the phenomena can not be explained by the character of the surface of the solid particles, but rather

by the effect of the preferential adsorption of hydroxyl ions and the consequent adjustment of interfacial relations between the liquid and the solid phases. The hydroxyl, in the case of the frit, is no doubt derived from the water-quenching in manufacture and from the moisture of the atmosphere in storage. The alkali apparently produces a slight coagulation or flocculation of the grains, causing the alcohol to become entrapped in the interstices in such a way that it is less effective as a suspending medium. The presence of the hydroxyl ions may greatly increase the number of molecules of liquid that each silicate particle can adsorb, thereby reducing the amount of free alcohol with consequent thickening of the slip.

The grinding was carried out in alcohol-water mixtures to determine whether or not it is necessary to use the pure alcohol to obtain satisfactory results. It was found that the characteristics of the slip and the drying action changed progressively as the water content increased from that observed with alcohol alone to that observed with water alone. Thus the greatest benefit is derived when the alcohol is not diluted.

Other organic liquids were substituted for ethyl alcohol. The alcohols all gave practically the same kind of slips. But benzene behaved differently. In the first place, the grinding action in this medium was extremely poor. The insoluble silicate was capable of taking up only a very limited amount of the liquid; that is, it was impossible to thin a benzene-mullite slip beyond a certain consistency, so rapid was the settling to a definite volume of the solid from the excess liquid. The situation was much the same with the partially soluble silicate, although the tolerance for the liquid was somewhat greater and settling out was not so rapid. In both cases so little of the benzene was retained by the suspension that it would scarcely flow after a few seconds. There was no tendency for either the soluble or the insoluble to cake, so in that respect benzene possesses an advantage over water.

Similar reactions were observed when xylene was used as the grinding medium. The grinding action was poor, and the settling to a definite maximum stable volume very rapid. This seems to be characteristic of nonpolar compounds.

III. Conclusions

To overcome the agglomeration, caking, and scumming encountered in the use of partially water-soluble silicate frits, certain organic grinding media may be used successfully. Polar compounds, such as alcohol, on account of their superior influence in grinding, are preferable.

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CERAMIC ABSTRACTS[1]

Compiled by the

AMERICAN CERAMIC SOCIETY

ROSS C. PURDY, Editor

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Vol. 12 **September, 1933** **No. 9**

Abrasives

Particle-size requirements in the abrasive industry. A. A. KLEIN. *Metal Cleaning & Finishing*, **5** [6], 261–62 (1933).—This discussion of equipment and methods developed to meet specifications for abrasive grains was presented in the symposium on "Industrial applications of particle-size measurement" held at the New York Regional Meeting of the A.S.T.M. A study of accurately punched plates with controlled uniform holes is expected to provide the accurate sieves necessary for master standards. E.J.V.

Grinding and polishing processes. L. HAMBURGER. *Z. Metallkunde*, **25** [2], 29–32; [3], 58–61 (1933).—The grinding and polishing processes are compared. The theory of polishing and the deformation and surface changes resulting from polishing are discussed. L.T.B.

Pedal operates grinder shield. B. TAYLOR. *Popular Sci. Monthly*, **122** [5], 68 (1933).—A practical shield for abrasive wheels is described and illustrated. F.G.H.

Measurement of polish in order to determine its bearing on corrosion of nonoxidizable steels. J. COURNOT AND L. HALM. *Compt. rend.*, **196**, 1017–18 (1933).—The coefficient of polish is defined as the ratio of the intensity of the light reflected at 45° to that of the direct ray; a method of measuring it photoelectrically is described. The results indicate the importance of the fineness of the polishing powder, and, in the case of coarse powders, the effect of the direction of polishing. (*B.C.A.*)

Stainless steel grinding and polishing. F. LEVERICK. *Iron & Steel Ind.*, March, 1933; abstracted in *Abrasive Ind.*, **14** [5], 20 (1933). W.W.M.

PATENTS

Process of making abrasive disks. A. J. DOERMANN. U. S. 18,872, June 20, 1933 (reissue). A bonded abrasive article comprises abrasive granules coated with a hardened Chinawood oil and bonded with a heat-hardened resin.

Design for abrading machine. A. N. EMMONS (Porter-Cable Machine Co.). U. S. 90,239, July 4, 1933.

Water-repellent abrasive. RUPERT S. DANIELS (Bakelite Corp.). U. S. 1,900,430, March 7, 1933. An abrasive implement for wet grinding has a porous structure prepared from abrasive particles bonded with a resinoid and impregnated with chlorinated naphthalene which is substantially free from mono- and dichlornaphthalenes.

Abrader or polisher for automobile bodies. JOHN VICIC. U. S. 1,913,574, June 13, 1933.

Honing machine for piston pinholes. JOSEPH SUNNEN. U. S. 1,913,689, June 13, 1933.

Balanced abrasive wheel. J. J. O'SULLIVAN (J. P. Conway). U. S. 1,913,852, June 13, 1933.

Process and apparatus for grading abrasives. J. C. PARKINSON AND FREDERICK GELSTHARP (Pittsburgh Plate Glass Co.). U. S. 1,914,039, June 13, 1933.

Cam-grinding apparatus. W. F. FRASER (Norton Co.). U. S. 1,914,561, June 20, 1933.

Grinding measuring device. W. GROTHKOPP. U. S. 1,914,565, June 20, 1933.

Method for finish grinding and polishing. C. T. RAULE. U. S. 1,914,647, June 20, 1933.

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[1] The abbreviation (*C.A.*) at the end of an abstract indicates that it was obtained from *Chemical Abstracts* by cooperative agreement.

The bold-face number following the journal name is the volume, the issue number is in brackets, followed by the page numbers, then the year in parentheses.

Machine for grinding disk knives. F. O. BENNETT (New York Mills Corp.). U. S. 1,914,879, June 20, 1933.

Grinding machine. W. J. GUILD (Heald Machine Co.). U. S. 1,914,995, June 20, 1933. W. N. APPLETON (McKay Co.). U. S. 1,915,144, June 20, 1933. H. W. MILLER. U. S. 1,916,063, June 27, 1933. CLEMENT BOOTH (Heald Machine Co.). U. S. 1,916,916 and 1,916,917, July 4, 1933.

Grinding tool. J. K. E. DIFFENDERFFER (Carr-Lowrey Glass Co.). U. S. 1,915,016, June 20, 1933.

Method and machine for grinding in valves and cocks. KARL MARTIN. U. S. 1,915,195, June 20, 1933.

Work-holding device for grinding machines. J. J. HOLLOWAY AND L. E. LINSLEY (Stanley Works). U. S. 1,915,247, June 20, 1933.

Stropping machine for razor blades. T. C. SHEEHAN (Wade & Butcher Corp.). U. S. 1,915,477, June 27, 1933.

Grinding machine for razor blades. T. C. SHEEHAN (Wade & Butcher Corp.). U. S. 1,915,478, June 27, 1933.

Gear-polishing machine. T. J. MULLEN AND W. C. POWELL (City Machine & Tool Works). U. S. 1,915,749, June 27, 1933.

Method and device for finishing taper rolls. W. E. HOKE. U. S. 1,915,789, June 27, 1933.

Method of refinishing engine cylinders. O. A. DAHLBERG (Joseph Sunnen). U. S. 1,915,817, June 27, 1933.

Grinding machine for crank shafts. H. J. ERIKSEN. U. S. 1,915,853, June 27, 1933.

Method and apparatus for classifying abrasives suspended in liquids. LUCIEN BERGUERAND (Soc. anon. des manufactures des glaces et produits chimiques de St.-Gobain, Chauny et Cirey). U. S. 1,916,035, June 27, 1933.

Lapping machine. A. E. ROBINSON (American Tool Works Co.). U. S. 1,916,117, June 27, 1933. A. E. ROBINSON AND W. G. HOELSCHER (American Tool Works Co.). U. S. 1,916,118, June 27, 1933.

Apparatus for grinding gun barrels and cylindrical surfaces. M. C. HUTTO (Hutto Engineering Co.). U. S. 1,916,267, July 4, 1933.

Cylinder grinding stand. W. A. JENNINGS (Rapid Tool Corp.). U. S. 1,916,618, July 4, 1933.

Buffing wheel. E. W. HALL. U. S. 1,916,759, July 4, 1933.

Valve grinding machine. B. T. STEBER. U. S. 1,916,775, July 4, 1933.

Control mechanism for machine tools. A. F. BENNETT (Brown and Sharpe Mfg. Co.). U. S. 1,916,914, July 4, 1933.

Combination lapping and testing machine for gears. B. J. WOLFE (Gleason Works). U. S. 1,917,178, July 4, 1933.

Abrading and scouring roll. ERNEST HOPE (United Shoe Machinery Corp.). U. S. 1,917,303, July 11, 1933.

Device for applying abrasive tool covers. FRED RICKS AND E. F. TOWNDROW (United Shoe Machinery Corp.). U. S. 1,917,329, July 11, 1933.

Apparatus for grinding wood. C. O. BACHMAN (Mead Research Engineering Co.). U. S. 1,917,420, July 11, 1933.

Cutter grinder. F. W. CURTIS (Kearney & Trecker Corp.). U. S. 1,917,504, July 11, 1933.

Breaker-point grinder. H. H. WALTERS. U. S. 1,917,863, July 11, 1933.

Mounting for hand grinding device. LUIS SCHULTE (Allegheny Steel Co.). U. S. 1,917,906, July 11, 1933.

Internal grinding apparatus. G. G. AGOSTONI. U. S. 1,918,077, July 11, 1933.

Carriage positioning mechanism for grinding machines. B. F. STOWELL (Van Norman Machine Tool Co.). U. S. 1,918,147, July 11, 1933.

Grinding or polishing machines. CHICAGO PNEUMATIC TOOL CO. Brit. 393,184, June 8, 1933.

Work holders for blade-grinding machines. F. W. BURROWS AND A. GREEN. Brit. 393,829, June 21, 1933.

Grinding and polishing facets on rotary bodies. J. DESENBERG. Brit. 394,142, June 28, 1933.

Process for the manufacture of waterproof abrasive articles and devices relating to it. Z. HADNAGY, A. BOUILLARD, AND A. AUBY. Brit. 394,442, July 5, 1933.

Method and machine for abrading work pieces. HEALD MACHINE CO. Brit. 394,563, July 5, 1933.

Abrasive disks. M. SPIRA. Belg. 391,274, Oct. 31, 1932. The disks are produced

by molding under pressure a paste composed of abrasive grains (corundum, silicon carbide), MgO, S_2Cl_2, and colza oil. See also *Ceram. Abs.*, **11** [7], 398 (1932). (*C.A.*)

Regulating pressure of sheet glass grinding tools. C. HEUZE. Ger. 558,209, Jan. 31, 1930. A constant counterweight mounted on a swinging arm exerts pressure on the tool through a curved guide, the curvature being a function of the pressure to be relieved. (*J.S.G.T.*)

Abrasive compositions. DEUTSCHE CARBORUNDUM-WERKE G.M.B.H. Ger. 571,436, Nov. 7, 1930. Abrasive grains are mixed with the products obtained by treating rubber with concentrated H_2SO_4, an organic sulfonic acid, or sulfonyl chloride, and the mixture is molded and then hardened by heat. Rubber, resins, and (or) comminuted fibrous materials may be added to the mixture. Cf. Ger. 487,776 (*C.A.* **24**, 2007). (*C.A.*)

Art and Archeology

Progress report on research in tableware design. A. E. BAGGS. *Bull. Amer. Ceram. Soc.*, **12** [7], 227–28 (1933); see also article by Bogatay and Baggs, *Ceram. Abs.*, **11** [3], 150 (1932).

Lithographs as a means of pottery decoration. ANON. *Pottery Gas.*, **58** [672], 701–15 (1933).—A thorough discussion of the question "Can ceramic transfers successfully yield all the qualities demanded by good and reliable pottery?" by debates conducted at the May meeting of the North Staffordshire Branch of the Society of Industrial Artists is presented. E.J.V.

Ladies pictured in porcelain. ANON. *Arts & Dec.*, **39** [2], 18–19 (1933).—A group of feminine figures by Mrs. Railston demonstrates how a rigid medium may be made softly graceful with dextrous handling. E.B.H.

Art news. ANON. *Design*, **34** [11], 271–72 (1933).—Art News mentions (1) an exhibition by the N. Y. Society of Ceramic Arts at the Art Center in March with talks on "Flower arrangements as related to pottery containers," "Prehistoric Greek pottery," "The theory and practice of glazes," and (2) the Robineau Memorial Ceramic Exhibition open to potters of the U. S., held at the Museum of Fine Arts, Syracuse, N. Y., during May. E.B.H.

Passing of an ancient art. R. H. JENKINS. *Design*, **34** [11], 256–59 (1933).—J. describes the process of throwing on the wheel, showing many illustrations of the various stages and working drawings of 2 kick wheels. E.B.H.

History of the York school of glass painting. JOHN A. KNOWLES. *Jour. Brit. Soc. Master Glass Painters*, **4** [3], 146–55 (1932).—K. discusses the Cistercian influence on the design of York glass. Illustrated. M.V.K.

Islamic art. J. GRELL. *Tonind.-Ztg.*, **57** [48], 555–57 (1933).—Ceramic materials have been used since the beginning of Islamism. A large collection of ceramic products is found in the Berlin museum which has been reorganized recently. The collection is described in some detail. W.M.C.

Dating Ming blue and white. LEIGH ASHTON. *Connoisseur*, **91** [381], 283–93 (1933).—The article is a contribution toward solving a standing problem. Reasons are advanced for suggesting the invention date as the Yuan dynasty (A.D. 1279 to 1368). Illustrated. E.B.H.

Prehistoric pottery and the beginning of the iron age. KARL MOSSLER. *Illus. London News*, **182**, 542–43 (1933).—The first iron age is dated from Hallstatt, Upper Austria. Its influence on contemporary pottery was to make the pottery much lighter and more graceful in imitation of the metal ware. 10 photographs. H.H.S.

Grave at Mapungabwe, Transvaal. F. R. PAVER. *Illus. London News*, **182**, 494–95 (1933).—The pottery bowl for food under the skeleton's arm is finished black with graphite and is far finer than any modern native work. The grave also contained much gold work. H.H.S.

BOOKS

Ancient Stained and Painted Glass. F. SYDNEY EDEN. Cambridge Univ. Press, 1933. Price 8s 6d. Reviewed in *Notes & Queries*, **164**, 288 (1933). H.H.S.

Noted Porcelains of Successive Dynasties. HSIANG YUAN-PIEN. Reviewed with illustrations in *Discovery*, **14**, 161–64 (1933); for review see *Ceram. Abs.*, **11** [3], 153 (1932). H.H.S.

PATENTS

Design for tumbler. J. N. MCNASH (Hazel-Atlas Glass Co.). U. S. 90,120 and 90,121, June 13, 1933.

Design for jar. G. A. MENGLE (Brockway Sales Co.). U. S. 90,122, June 13, 1933. IVOR CORDY (Hazel-Atlas Glass Co.). U. S. 90,176, June 20, 1933. O. C. NOBLE (Tygart Valley Glass Co.). U. S. 90,208 and 90,209, June 27, 1933. FRASIER SMITH (Hazel-Atlas Glass Co.). U. S. 90,268, July 4, 1933. H. R. MCDONALD (Hart Glass Mfg. Co.). U. S. 90,290, July 11, 1933.

Design for bottle. FRASIER SMITH (Hazel-Atlas Glass Co.). U. S. 90,216, June 27, 1933.

Design for lens for automobile head lamps. NICOLAS DE LEO. U. S. 90,237, July 4, 1933.

Apparatus for reading colors. E. S. BODINE (Shell Petroleum Corp.). U. S. 1,914,937, June 20, 1933.

Decoration of pottery articles. V. G. H. ALCOCK, R. B. BLOORE, W. S. LINDLEY, AND P. R. BURT. Brit. 392,767, May 31, 1933.

Gilding ceramic ware. DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORM. ROESSLER. Ger. 558,847, March 31, 1929. Powdered golds which are tinted by the presence of other metals, such as Ag, Cu, and Bi, contain metals of higher thermal stability such as Rh, Cr, and Cl added as alloys or by electrolytic means. (*J.S.G.T.*)

Cements

Attempts to standardize the setting temperatures of cements. S. HERZ. *Tonind.-Ztg.*, **56** [98], 1204 (1932).—The heat developed during the setting of cement and concrete may result in internal strain and cracking of the building. Probst found an increase of temperature from 20 to 31°C in a large dam completed recently. The heat of setting has been determined for cements of different composition using a calorimeter. From the data obtained the heat which is developed by the different constituents of the cement is calculated. The amounts of tricalcium aluminate and tricalcium silicate are the most important factors in the heat development during the setting period. All other constituents have only a small influence. Heating diagrams have been drawn for the heat developed by given amounts of Al and Si. The results of American and German experiments agree very well. The specifications for the Pine Canyon dam allowing the use of cement containing not more than 6% tricalcium aluminate are discussed. W.M.C.

Recast analysis and its relation to the chemistry of Portland cement. XI. Computation of Portland cement raw mixtures. LOUIS A. DAHL. *Rock Prod.*, **36** [5], 24–26 (1933).—D. concludes his presentation of algebraic and graphic methods for computing cement raw mixtures, giving examples. A correction of a previous installment is included. This is the concluding article of the series. For Part X see *Ceram. Abs.*, **12** [8], 291 (1933). W.W.M.

Lime content of cement. H. KÜHL. *Tonind.-Ztg.*, **57** [40], 460–64 (1933).—Present knowledge of the rôle of lime in cement is reviewed. The maximum amount of lime found in cement may be derived from the formula $CaO = 2.8\ SiO_2 + 1.1\ Al_2O_3 + 0.7\ Fe_2O_3$. See also *Ceram. Abs.*, **12** [6], 215 (1933). W.M.C.

Progress in cement research. W. GRAF CZERNIN. *Tonind.-Ztg.*, **57** [40], 459–60 (1933). W.M.C.

Decomposition of cements in sea water. HENRY LE CHATELIER. *Age Ciment*, Oct., 1932; *Rock Prod.*, **36** [5], 26 (1933). W.W.M.

Book Review

Gypsum and Its Investigation. P. P. BUDNIKOFF. 2d ed. Published by Acad. Science, Leningrad, U.S.S.R., 1933. 6 R. This book is divided into two parts: The first is devoted to the literature of gypsum and includes (1) the general characteristics of gypsum, (2) anhydrite, (3) occurrences, (4) physical and chemical properties of gypsum, (5) gypsum modifications, (6) soluble and insoluble anhydrite, and (7) applications of gypsum and its setting agents. The second part is devoted to the results of researches made by B. from 1918 to 1932, and deals mostly with the questions of obtaining Portland cement from gypsum, anhydrite, and "clinkerless cement," and anhydrite and dolomite cement, and the action of some gaseous substances on $CaSO_4$ at high temperatures. M. V. KONDOIDY

PATENT

Manufacture of high-alumina cement. J. D. MORGAN (Doherty Research Co.). U. S. 1,913,943, June 13, 1933.

Enamels

Determination by X-ray methods of crystalline compounds causing opacity in enamels. A. I. ANDREWS, G. L. CLARK, AND H. W. ALEXANDER. *Jour. Amer. Ceram. Soc.*, **16** [8], 385–92 (1933).

Manufacture of porcelain or vitreous enamel on sheet iron. GLENN A. HUTT. *Enamelist*, **10** [8], 10 (1933).—H. gives the history and a detailed description of all the operations involved in porcelain or vitreous enameling. W.W.M.

Heat reactions in the treatment of cast iron with soda ash. J. K. SMITHSON AND J. E. FLETCHER. *Foundry Trade Jour.*, **48**, 266, 332 (1933).—The addition of soda ash to cast iron (see article by Evans, *Ceram. Abs.*, **12** [5], 182 (1933)) removes silicon as well as sulfur. The ratio of these removals under differing conditions and the heat reactions involved are discussed. H.H.S.

Acid-proof enameled apparatus. VI. V. LOKSHIN. *Khimstroi*, **5**, 2035–37 (1933).—An acid-proof enamel with chemical, physical, and mechanical properties suitable for use on chemical apparatus was developed, having the molecular formula, $0.75Na_2O{\cdot}0.25CaO{\cdot}0.075Al_2O_3{\cdot}2.8SiO_2{\cdot}0.08B_2O_3{\cdot}0.2F_2$, which corresponds to the composition, 527 sand, 65 kaolin, 57 borax, 85 $CaCO_3$, 230 Na_2CO_3, and 42 Na_2SiF_6. Comparative tests with 5 g. powdered and sifted enamels by boiling 20 hr. with 100 cc. 10% HCl and HNO_3 produced a loss of weight of 0.0015 g. for the above enamel and 0.086 to 0.132 g. for the best French and German products; the latter soften and lose luster on heating more readily than the former. The experiments show that the lowering of the melting point does not reduce the stability; by substitution of Al_2O_3 for SiO_2 the resistance to alkalis is improved; the influence of oxides on the stability of enamels is, in increasing order, ZnO, CaO, MgO, and BaO. (*C.A.*)

Examination of structures up to 1100°C. H. ESSER AND H. CORNELIUS. *Stahl Eisen*, **53** [20], 532–35 (1933).—An arrangement has been developed for microscopic studies up to 1100°C. A number of micrographs is given showing the α-γ transformation of pure iron, the austenite-martensite transformation in chilled steel containing 2% carbon and 2% manganese, the formation of temper-carbon in steel, and the solution of oxygen in electrolytic iron as a function of the temperature. No dissolving of iron oxides in solid iron has been detected by microscopic investigations. W.M.C.

X-rays in the metal industries. R. A. STEPHEN. *Metallurgia*, **8** [44], 35–36 (1933).—Examination of work by X-rays is one of the most important testing methods. In this paper its scope in industries is discussed and some apparatus is described. M.V.K.

X-ray examinations of iron and steel. F. WEVER. *Stahl Eisen*, **53** [19], 497–505 (1933).—X-ray machines and X-ray tubes have been developed which will give satisfactory results. Much work has still to be done in correlating X-ray data and actual service value of the metals. It is possible to measure internal strain accurate within ±1.5 kg./sq. mm. by means of X-rays. Very sensitive methods allow the measurement of small lattice distortions such as are caused by the cold working of metals. W.M.C.

Enameling furnaces with floating-flue muffles. H. C. JURS. *Better Enameling*, **4** [5], 14 (1933).—J. describes a type of furnace which he designed to reduce the hazard of leaky muffles resulting from repeated heating and cooling, to reduce fuel consumption if possible, and to increase the heat radiating surface within the firing chamber. Two detailed drawings are presented and the operating results, which have been excellent over a two-year period, are given. For patent see *Ceram. Abs.*, **12** [3], 124 (1933). W.W.M.

Photoelectric relay on conveyer reduces enamel rejects. R. B. REID. *Ceram. Ind.*, **20** [6], 277 (1933).—A photoelectric relay, operating through a set of mirrors, controls a chain conveyer at the plant of the National Enamel & Stamping Co. W.W.M.

Prefabricated enameled walls used with sanitary ware. GEORGE SAKIER. *Ceram. Ind.*, **20** [6], 286 (1933).—S. has designed for the American Radiator and Standard Sanitary Corp., a series of bathroom panels in which the sanitary ware fixture and a section of enameled steel wall are included in one unit. This simplifies the designing, building, or remodeling of the bathroom. Panels include every variety of fixture for the bathroom. W.W.M.

Porcelain enamel store front. BERNARD J. GARRY. *Enamelist*, **10** [9], 14–15 (1933).—This is the first of a series of articles on methods used in building porcelain enamel store fronts, houses, etc. Photographic illustrations and detailed drawings are included. W.W.M.

Problem of lead-bearing enamels. ANON. *Amer. Enameler*, **6** [3], 3–4 (1933).—

Lead poisoning of workers in plants using lead-bearing enamels and the possibility of lead poisoning from utensils coated with this material are discussed. It is safe to assume that there is absolutely no danger of poisoning from use of utensils enameled with acid resisting lead-bearing enamels. W.W.M.

Ten years' progress in porcelain enameling. E. R. BRAUNER. *Ceram. Ind.*, **21** [1], 20–22 (1933).—B. cites the progress during the past ten years of the various phases of the enameling industry. W.W.M.

BOOK

Textbook of Metallurgical Problems. A. BUTTS. McGraw-Hill Book Co., New York, 1932. xiv + 425 pp. Price $4.00. *Jour. Inst. Metals*, **53** [3], 173 (1933). F.G.H.

PATENTS

Enamel-firing fixture. J. WINKLER (Ohio Foundry Co.). U. S. 1,913,623, June 13, 1933.

Firing rack. H. T. BEBB (Canton Stamping & Enameling Co.). U. S. 1,914,967, June 20, 1933.

Tiled construction. O. E. GRIGSBY (Porcelain Tile Corp.). U. S. 1,916,136, June 27, 1933.

Metal wall tile fastening. A. W. NELSON (Columbian Enameling & Stamping Co.). U. S. 1,917,388, July 11, 1933.

Metal tile wall structure. H. R. SPENCER (Porcelain Tile Corp.). U. S. 1,918,228, July 11, 1933.

Glass

Release of strain in glass. JAMES BAILEY AND D. E. SHARP. *Jour. Amer. Ceram. Soc.*, **16** [8], 367–79 (1933).

Color changes in flint glass. A. K. LYLE AND D. E. SHARP. *Jour. Amer. Ceram. Soc.*, **16** [8], 380–84 (1933).

Influence of grain size of raw material on glassmelting. ANON. *Keram. Rund.*, **40**, 648–50 (1932).—In general practice, a sand of medium grain size, ranging from 0.1 to 0.5 mm., is most suitable; in sulfate melts a better result is obtained with a somewhat finer sand, from 0.1 to 0.3 mm. Mineral raw materials of a refractory nature and any component that constitutes only a small proportion of the batch require very fine grinding. (*J.S.G.T.*)

Permeability of glass and fused quartz to ether, alcohol, and water at high pressures. T. C. POULTER AND R. O. WILSON. *Phys. Rev.*, **40**, 877 (1932).—Pressure windows will withstand several times the pressure when oil or glycerine are in contact than if water, alcohol, or ether are employed. A sample to be tested, consisting of a quartz or glass rod 3 to 4 mm. in diameter and 15 mm. long, was placed in a piece of rubber tubing 5 cm. long and 6 mm. in diameter containing the liquid and stopped at both ends. This was put under pressure in a pressure cylinder. Oil and glycerine produced no fractures but with water, alcohol, or ether fractures were obtained if a pressure of about 15,000 atmospheres was maintained for 5 min. or more and suddenly released. Glass and quartz behaved about the same. Breakage generally occurred on releasing the pressure. A piece of glass having oil in contact with one side and water with the other is fractured on the latter side only. D.E.S.

Cerium, selenium, and their compounds in the glass industry. OTTO R. HERFURTH. *Diamant*, **55** [6], 62–64; [7], 74–75 (1933).—H. discusses the chemistry of selenium, cerium, and decolorizers operating both physically and chemically. He discusses black selenium, red selenium, sodium selenide, zinc selenide, and selenium as a coloring medium and as a decolorizing medium. E.J.V.

Effect of barium oxide on properties of technical glasses. F. H. ZSCHACKE, W. HÖFLER, AND A. RIAZA. *Keram. Rund.*, **40**, 534–36, 558–61 (1932); *Chem. Zentr.*, **i**, 103 (1933).—In glasses with 10% RO, substitution of CaO by BaO raises the speed of melting. The clarifying velocity at first increases and then decreases; the glasses are "longer." Pure BaO glass is almost colorless; the workability and the luster are improved by BaO. On substitution of Na_2O by BaO the melting velocity is at first almost unchanged, but larger quantities reduce it; clarification is more difficult and the color is darker. BaO glasses poor in Na_2O readily devitrify. Prolonged melting produces a brown color due to sulfide. (*B.C.A.*)

Strange instance of the attack of sulfuric acid on a bottle glass. L. Farcy. *Ann. fals.*, No. 281, p. 290 (1932).—A green bottle containing sulfuric acid for accumulators was found after storage to be shattered, the pieces retaining their place, however. The inner surface was covered irregularly by a mass of crystals and flakes matted together. Cavities or geodes were filled with crystals. The whitish mass had the following percentage composition: H_2O 24.7, loss on ignition 4.0; SiO_2 35.7, FeO 0.29, Al_2O_3 1.68, CaO 16.4, MgO 1.44, K_2O 7.73, SO_3 8.39, and free acid as SO_3 6.26. The white mass swelled on heating assuming a spongy appearance like calcined alum. Some of the crystals consisted of potash alum. (*J.S.G.T.*)

Solubility of lead glasses in relation to their alkali content. Oskar Knapp. *Jour. Soc. Chem. Ind.* [Japan], **35** [11], 520–22*B* (1932).—K. reviews and discusses the results of investigations of Turner (*Ceram. Abs.*, **3** [3], 68 (1924)), Peddle (*ibid.*, **1** [12], 329 (1922); *Glass*, p. 45 (1926)), Tabata and Yegami (*Ceram. Abs.*, **9** [2], 90 (1930)), and Karmaus (*ibid.*, **6** [8], 336 (1927)) dealing with the solubility of lead glasses. Because of the variation in these results, it is premature to fix a general rule for the solubility and weathering of lead glasses. It is necessary to carry on systematic investigations to determine whether the influence of sodium and potassium oxides on the solubility in water is equal or different. M.V.K.

Solubility of clays in alkaline solutions. Kyu-hei Kobayashi and Ken-ichi Yamamoto. *Jour. Soc. Chem. Ind.* [Japan], **35** [11], 522–23*B* (1932).—The solubility of clays in various concentrations of alkaline solutions was studied in order to determine their chief components. About 70 samples of various clays were tested. M.V.K.

Slag nepheline glass. A. N. Dauvalter. *Keram. i Steklo*, **9** [3], 26–27 (1933).—D. describes attempts made to manufacture glass from nepheline and slag. The slag employed was a slag obtained in the production of phosphorus, and contained 53% SiO_2, 36% CaO, some admixtures, and alkalis. The glass melted easily, was easily worked and purified, and had no tendency to devitrification. The glass was bottle green. M.V.K.

Adsorption of gases by glass. IX. Nitrous oxide. M. Crespi. *Anales soc. españ. fís. quím.*, **30**, 520–27 (1932).—The adsorption of N_2O on glass at 16° between 253 and 760 mm. was measured. The correction to be applied to vapor density measurements in a 1-liter vessel is about 6×10^{-5} g. The adsorbed film is probably unimolecular. For Parts VI to VIII see *Ceram. Abs.*, **10** [10], 685 (1931). (*J.S.G.T.*)

Consideration of glass beakers. F. Friedrichs. *Glas App.*, **13**, 187–90 (1932).—Glass beakers of the four principal forms, *i.e.*, Thüringer, Griffin, high, and low, are classified. Complete tables are given of the volume, diameter, height, etc. The ratios of diameter to height are 1:2, between 1:2 and 1:1.6, between 1:1.6 and 1:1.2, and between 1:1.2 and 1:0.7 for the four forms, respectively. The possibility of the standardization of sizes is discussed. (*J.S.G.T.*)

Notes on the luminescence of glass and fluorite. Theodore Lyman. *Phys. Rev.*, **40**, 578 (1932).—A simple method is described for showing the relation between absorption of light and luminescence, the apparatus required being a small quartz spectrograph and a condensed, metallic-electrode spark. Most of the observations concern clear and colored fluorite and quartz. D.E.S.

Surface phenomena of glass. A. Bergmann. *Metallbörse*, **23**, 493–95 (1933).—A review of literature on surface effects of glass includes the production of mat surfaces by sandblasting or etching with HF preparations. The microscopic pseudocrystalline appearance of etched surfaces is explained. Other surface effects are due to devitrification produced by working in a flame and that which appears in ancient glass, adsorption of gases, weathering by exposure to the atmosphere, and reaction with dyes such as methylene blue. (*C.A.*)

Study of the durability in relation to the composition of crucibles used for glass. Experiment on the durability of crucibles for a borosilicate glass. Saigiro Kinya. *Repts. Imp. Ind. Research Inst., Osaka, Japan*, **13**, Part 2, 27 pp. (1932).—Instead of soda glass (*ibid.*, No. 9, Part 6 (1928)) borosilicate glass was used. Twenty crucibles (domestic and foreign) were compared. The smaller the porosity of the crucibles the greater the durability for melting the glasses. To obtain the smallest possible porosity of crucibles it was necessary either to raise the temperature, to add some feldspar to the raw material, or to choose raw material containing some marble. Crucibles high in alumina and prepared at a high temperature are more durable and have less porosity for H_3BO_3 than those high in silicic acid. (*C.A.*)

Fusion of crystal and glass. A. Thouvenin. *Céram. Verrerie*, No. 841, pp. 367–70; No. 842, pp. 419–22; No. 843, pp. 479–82; No. 844, pp. 545–47; No. 845, pp. 603–607 (1932).—The fusion of crystal and window glass is studied from a physical-chemica

standpoint. Calculations are made and explained and graphs are plotted showing (1) the progress of fusion with and without cullet, from which other curves may be drawn for any mixture of cullet and raw batch; (2) the temperature of the glass in various portions of the pot and the total calories absorbed in each portion; and (3) the time required for refining as dependent upon the viscosity of the glass and the resulting velocity of the gaseous bubbles. By the aid of these curves the glassmaker may trace the progress of the fusion of the batch by knowing only the temperature. M.H.B.

New ideas and methods of glassmelting. II. S. S. BERMAN. *Keram. i Steklo*, **9** [3], 19–23 (1933).—B. discusses attempts to use vertical kilns for melting glass. Several kilns are described. For Part I see *Ceram. Abs.*, **12** [7], 258 (1933). M.V.K.

Protective glasses for the welding technicians. G. ROSE. *Diamant*, **55** [10], 109–10 (1933).—R. discusses various glasses which are available for welders to protect them against the injurious ultra-violet and infra-red rays developed at welding temperatures. The specific glasses suitable for different types of welding are listed. E.J.V.

Testing of ampoule glasses. G. DULTZ. *Pharm. Ztg.*, **78**, 482–83 (1933).—In the standard "alkalinity" test (autoclaving the ampoule filled with HCl–Me-red solution until the color changes) no allowance is made for the greater specific surface exposed by the smaller ampoules. Tables are given showing the concentration of acid which must be used for the various sizes in order to obtain strictly comparable results. (*B.C.A.*)

Contribution to the question of determining the most economical type of furnace for flat and hollow glass painting. J. F. KESPER. *Diamant*, **54** [35], 469–70 (1932).—K. discusses the various types of furnaces best suited for flat and hollow glass painting and for glass bending, pointing out the economical features of each. E.J.V.

Glass-stamping machines. OTTO R. HERFURTH. *Diamant*, **55** [5], 52–54 (1933).—H. discusses briefly the various types of glass-stamping and decorating machines, taking them up as a general class, for manual operation, and for automatic operation. Illustrated. E.J.V.

Glass is a lobster. F. W. PRESTON. *Glass Ind.*, **14** [6], 68–69 (1933).—P. discusses the definition of glass as "an undercooled liquid" from several different angles, pointing out how difficult it is to define accurately the true status of a glass. Citations of statements from work by various physical chemists on glasses are used to show wherein the practical man and the theoretical man vary in their explanations of various phenomena. E.J.V.

New glass mosaics. F. H. *Diamant*, **55** [8], 87–88 (1933).—H. describes and discusses some of the more recent examples of stained glass mosaic work and some of the contemporary stained glass artists. E.J.V.

Glass as an interior architectural element. J. WOLF. *Diamant*, **55** [13], 147–48; [14], 150 (1933).—W. discusses the use of glass as art windows, both stained and unstained, and as a wall covering or decoration indoors. The wall covering can be in the form of a stained glass mosaic or in the form of an imitation marble made of glass. The general adaptability of modern glass as an architectural medium is stressed. See also *Ceram. Abs.*, **12** [1], 15 (1933). E.J.V.

Glass manufacture in England. G. MARCHAND. *Times Eng. Supp.*, **32**, *Supp. "Constructive Economics,"* May 6, 1933.—Mechanization, the introduction of continuous processes in the main branches of the industry, is discussed with especial reference to colored opaque glasses, glass in buildings and for motor cars, heat-insulation glass, bottle, table, and fancy glass, and illuminating ware. H.H.S.

Manufacturing watch glass at the Chassteklo works. I. E. IVANOV. *Keram. i Steklo*, **9** [3], 11–12 (1933).—A detailed description of the manufacture of glass for watches is given. M.V.K.

Utilization of "podzol" in the Krasnodarski glassworks. P. N. PROSTOV. *Keram. i Steklo*, **9** [3], 7–9 (1933).—"Podzol," a waste product in the production of potash, contains alkalis and alkaline-earth oxides and can be used as a raw material in the glass industry. Experiments at the Krasnodarski works showed that it can replace alkalis and chalk. The results were satisfactory. M.V.K.

Ten years' progress in the glass industry. JOHN W. ROMIG AND J. C. HOSTETTER. *Ceram. Ind.*, **21** [1], 17–20 (1933).—The authors review the history of each phase of the glass industry during the past ten years. W.W.M.

Wallpaper made of spun glass. ANON. *Popular Sci. Monthly*, **122** [5], 40 (1933).—Wallpaper made from fine spun-glass fibers on a paper foundation is described and illustrated. F.G.H.

Roman glass. L. M. ANGUS-BUTTERWORTH. *Glass Ind.*, **14** [6], 65–68 (1933).—Rome obtained its first glass from Egypt shortly after 26 B.C., and in 14 A.D. the indus-

try was established at Rome itself. The various developments of Roman glass are discussed in this excellent historical treatment of the subject. The greatest triumph of the Romans in glass was in the production of their cut or sculpture pieces such as the Portland or Barberini Vase, the Naples Vase, and the Auldjo Vase, each of which is described in detail. E.J.V.

Third British Glass Convention. ANON. *Pottery Gaz.*, **58** [672], 721–35 (1933).—A complete report of the Convention held at Buxton, May, 1933, is given. Illustrated. E.J.V.

BOOKS

Calibration and Standardization of Chemical Glassware. (Eichung und Normung chemischer Glasgerate.) F. FRIEDRICHS. Verlag "Glas und Apparat," R. Wagner & Sohn, Weimar, Germany, 1933. 24 pp. Price 3 Rm. *Jour. Amer. Chem. Soc.*, **55** [6], 2620 (1933). F.G.H.

Glass Manufacture. Vol. II. ROBERT DRALLE. *Z. phys. Chem.*, **A, 162** [4–5], 382–83 (1933); for abstract see *Ceram. Abs.*, **11** [5], 302 (1932). L.T.B.

PATENTS

Take-off and leering conveyer for sheet-glass forming machines. EUGÈNE GENTIL (American Bicheroux Co.). U. S. 18,881, June 27, 1933 (reissue).

Installation for the manufacture of glassware. W. J. MILLER (W. J. Miller, Inc.). U. S. 1,913,501, June 13, 1933.

Charging apparatus. R. L. FRINK. U. S. 1,913,665, June 13, 1933.

Pot-making apparatus. R. M. BRASKET (Pittsburgh Plate Glass Co.). U. S. 1,914,004, June 13, 1933.

Wire netting for wire glass. JAMES CARRIE (F. W. Preston). U. S. 1,914,007, June 13, 1933.

Apparatus for fabricating glassware. K. E. PEILER (Hartford-Empire Co.). U. S. 1,914,155, June 13, 1933.

Apparatus for feeding molten glass. K. E. PEILER (Hartford-Empire Co.). U. S. 1,914,156, June 13, 1933.

Method and apparatus for forming glassware. K. E. PEILER (Hartford-Empire Co.). U. S. 1,914,157, June 13, 1933. J. E. MCLAUGHLIN, J. H. TREECE, AND L. D. SOUBIER (Owens-Illinois Glass Co.). U. S. 1,917,140, July 4, 1933.

Manufacture of blown glassware. G. E. ROWE (Hartford-Empire Co.). U. S. 1,914,169, June 13, 1933.

Machine and method of shaping silica, etc. I. F. HOOPER, B. F. NIEDERGESASS, AND P. K. DEVERS (General Electric Co.). U. S. 1,914,205, June 13, 1933.

Means for making laminated glass. A. G. WORRALL (Safetee Glass Co.). U. S. 1,914,392, June 20, 1933.

Safety glass. J. H. CLEWELL (Du Pont Viscoloid Co.). U. S. 1,915,048, June 20, 1933. B. C. BREN (Du Pont Viscoloid Co.). U. S. 1,915,085, June 20, 1933.

Apparatus for making corrugated wire glass. ARNO SHUMAN (Pennsylvania Wire Glass Co.). U. S. 1,915,255, June 20, 1933.

Glass-defrosting tray for mechanical refrigerators. A. C. CRIMMEL AND H. H. CRIMMEL (Sneath Glass Co.). U. S. 1,915,647, June 27, 1933.

Automatic glassblowing machine. A. C. PARKER (Libbey Glass Mfg. Co.). U. S. 1,915,836, June 27, 1933.

Illuminating apparatus. F. C. WINKLER (Westinghouse Electric & Mfg. Co.). U. S. 1,915,842, June 27, 1933.

Bottle-transferring mechanism. J. P. BENOIT (Owens-Illinois Glass Co.). U. S. 1,915,972, June 27, 1933.

Apparatus for glass feeding. S. G. STUCKEY (Obear-Nester Glass Co.). U. S. 1,916,155, June 27, 1933.

Method of producing tempered glass sheet. BERNARD LONG AND ROBERT TOUVAY (American Securit Co.). U. S. 1,916,174, June 27, 1933.

Glassware annealing leer. L. D. SOUBIER (Owens-Illinois Glass Co.). U. S. 1,916,178, June 27, 1933.

Machine for forming glass stoppers. L. D. SOUBIER (Owens-Illinois Glass Co.). U. S. 1,916,179, June 27, 1933.

Method and apparatus for feeding batch mixtures to furnaces. ROBERT GOOD (Hazel-Atlas Glass Co.). U. S. 1,916,262, July 4, 1933.

Method and apparatus for supplying glass to suction machines. W. T. HONISS (Hartford-Empire Co.). U. S. 1,916,666, July 4, 1933.

Method and apparatus for conditioning molten glass. G. E. HOWARD (Hartford-Empire Co.). U. S. 1,916,668, July 4, 1933.

Process and apparatus for applying edge-sealing material to laminated glass. T. G. WRIGHT (Duplate Corp.). U. S. 1,916,748, July 4, 1933.

Ornamental glass. FRANK CLARKE (Pittsburgh Plate Glass Co.). U. S. 1,916,753, July 4, 1933.

Apparatus for feeding batch mixtures to furnaces. ROBERT GOOD (Hazel-Atlas Glass Co.). U. S. 1,917,247, July 11, 1933.

Manufacture of wired glass. CHANCE BROS. & CO., LTD., AND A. L. FORSTER. Brit. 392,684, May 31, 1933, and 393,701, June 21, 1933.

Improved apparatus for supplying molten glass to machines for making glassware. SOC. ANON. D'ÉTUDES ET DE CONSTRUCTIONS D'APPAREILS MÉCANIQUES POUR LA VERRERIE. Brit. 392,832, May 31, 1933.

Vacuum-sealed canisters, bottles, jars, etc. E. GORE-LLOYD. Brit. 393,268 and 393,269, June 14, 1933.

Manufacture of nonsplintering glass. I. S. VIDAL. Brit. 393,406, June 14, 1933, and 393,760, June 21, 1933.

Process and apparatus for tempering glass. SOC. ANON. DES MANUFACTURES DES GLACES ET PRODUITS CHIMIQUES DE ST.-GOBAIN, CHAUNY ET CIREY. Brit. 393,491, June 14, 1933.

Apparatus for manufacturing plate glass, etc. COMPAGNIES RÉUNIES DES GLACES ET VERRES SPÉCIAUX DU NORD DE LA FRANCE. Brit. 393,841, June 21, 1933.

Manufacture of glass. E. HEINZ. Brit. 393,907, June 21, 1933.

Stratified bodies such as strengthened glass. TRIPLEX SAFETY GLASS CO., LTD., R. BOOTH, AND J. WILSON. Brit. 393,946, June 28, 1933.

Method of producing marbled glass surfaces. MAMMO-GLAS GES. AND G. SANDERSFELDT. Brit. 394,250, June 28, 1933.

Apparatus for supplying molten glass to machines for making glassware. SOC. ANON. D'ÉTUDES ET DE CONSTRUCTIONS D'APPAREILS MÉCANIQUES POUR LA VERRERIE. Brit. 394,282, June 28, 1933.

Method of preventing the blurring or dulling of sheet glass. MÜHLIG-UNION GLASINDUSTRIE AKT.-GES. Brit. 394,635, July 5, 1933.

Automatic suction machine for hollow glassware. W. BRAUER GEBR. GREINER. Ger. 513,054, Nov. 4, 1927. A parison mold is carried by an arm which is moved to and fro between the suction and working positions on an overhead track, the lowering and raising being actuated by rollers running on another suitably shaped track below. Other rollers similarly actuate the mold opening and closing mechanism. (*J.S.G.T.*)

Automatic suction machine. J. MAINZER. Ger. 543,049, Jan. 22, 1928. The arm bearing the suction mold is provided with means whereby the opening and closing of the mold is carried out without being affected by the swinging motion of the arm. (*J.S.G.T.*)

Automatic glassblowing machine. J. SCHÄFERS. Ger. 547,133, Nov. 4, 1930. The machine has a fixed inverted parison mold, fixed erect blow mold not disposed axially with the parison mold, and a plurality of neck molds rotating on a horizontal axis and capable of being rotated through 180° for the purpose of inverting the parison. (*J.S.G.T.*)

Rotation of reciprocating feeder plungers. W. J. MILLER. Ger. 555,612, March 17. The intermittent drive to the Miller feeder plunger is actuated by means of a reciprocating rack bar driving on either side a toothed wheel, each of which drives the plunger half a revolution by means of a pawl rotating idly on the other stroke. (*J.S.G.T.*)

Making holes in glass. C. FREY. Ger. 556,043, Sept. 9, 1930. A platinum point heated by benzol or other combustible vapor is used to make a hole through glass. (*J.S.G.T.*)

Shearing molten glass from a suction-fed parison mold. EUROPÄISCHER VERBAND DER FLASCHENFABRIKEN G.M.B.H. Ger. 556,098, Aug. 29, 1931. A knife attached to a baffle plate swinging below a suction mold is given a motion across the line of drop of the glass independently of the swinging of the arm carrying the baffle plate. (*J.S.G.T.*)

Apparatus for making laminated glass. DUPLATE CORP. Ger. 556,344, April 3, 1931. (*C.A.*)

"Regenerating" solarized U.-V. transmitting glass. CORNING GLASS WORKS. Ger. 556,717, Oct. 14, 1928. The glass is heated again to the annealing temperature. (*J.S.G.T.*)

Production of titanium glasses. I. G. FARBENINDUSTRIE A.-G. Ger. 556,895,

Oct. 24, 1929. The substitution of TiO_2 for SiO_2 and the use of alkali nitrate in the batch, which was melted at 1300°, are described. No precise details are given. (*J.S.G.T.*)

Production of quartz hollow ware. A. E. G. Ger. 557,204, Dec. 19, 1929. Quartz tubes heated at one end are rotated and blown out in molds suitably mounted and rotating in synchronism with the tubes. The molds are capable of movement vertically in the direction of the tube axes. (*J.S.G.T.*)

Feeding abrasive material to machines. E. Busch A.-G. Optische Industrie. Ger. 557,508, Jan. 27, 1931. Lens-grinding machines are provided with an annular trough containing an abrasive fluid in which the tool is dipped from time to time, the trough being movable in a vertical direction for the purpose. (*J.S.G.T.*)

Holding work while grinding and polishing. F. W. Kutzscher. Ger. 557,646, March 4, 1931. The device is adapted to hold vessels such as tumblers with conical inner surfaces by means of suction against a plate, being centered by a ring sliding under the action of a spring on an axis disposed centrally with respect to the plate. The whole outer surface of the vessel is thus free and can be worked on as desired. (*J.S.G.T.*)

Manufacture of double thick-walled vessels. Glasfabrik Sophienhütte R. Bock G.m.b.H. Ger. 560,331, Nov. 28, 1930. Double-walled vessels of substantial thickness are made by heating up the correctly disposed inner and outer components over a sufficiently wide area to distribute the stress, then uniting the edges of the two, and blowing out in a mold. (*J.S.G.T.*)

Take-in device. Thermal Engineering Corp. Ger. 560,384, April 29, 1928. The Shackelford take-in device is described. (*J.S.G.T.*)

Drawing glass from pots. Deutsche Spiegelglas A.-G. Ger. 561,169, May 8, 1931. The refractory member used inside the pot for the drawing operation is not made integral with the pot, but is separate, being introduced for the drawing process and then removed so that melting and refining can proceed again. See also Ger. 555,062, *Ceram. Abs.*, **12** [3], 105 (1933). (*J.S.G.T.*)

Felting glass threads. Firma O. Gossler. Ger. 561,213, May 13, 1931. The device comprises a stand and means for laying hanks of glass thread thereon lengthways to form layers and then transferring these layers as successive pads to a moving belt. (*J.S.G.T.*)

Controlling the flow of glass to rolls. Pilkington Bros., Ltd. Ger. 562,331, Oct. 6, 1932. The gate controlling the flow of glass down a feeder channel to the rolls is operated by a rod working in bearings permitting a flexing of the rod in the plane of the gate and linked to the latter. (*J.S.G.T.*)

Glass with strong U.-V. absorption and good visible transmission. Deut. Spiegelglas A.-G. Ger. 563,644, Dec. 24, 1929. Sheet and hollow glass are described which contain up to 10% of a mixture of rare-earth oxides in the proportions in which they occur naturally. (*J.S.G.T.*)

Controlling width of rolled sheet. Naamlooze Vennootschap Maatschappij tot Beheer en Exploitatie van Octrooien. Ger. 563,853, Oct. 27, 1932. The rolls are provided with distance rings capable of movement along the axes of the rolls so that the width of the space between the latter can be varied. (*J.S.G.T.*)

Joining tubes to glass bodies. Siemens-Schuckertwerke A.-G. Ger. 563,854, April 23, 1929. In addition to being rotated in its holder about the axis of the tube to be joined on, the glass body, such as a rectifying lamp bulb, is also provided with mechanical means for rotating about its own axis. (*J.S.G.T.*)

Machine for drawing glass. I. I. Zhukov. Russ. 27,998, June 16, 1930, and Jan. 16, 1931. Mechanical features are described. (*C.A.*)

Structural Clay Products

Brick for poured joints. C. Fred Sauerreisen. *Brick Clay Rec.*, **82** [6], 207 (1933).—A new type of brick with two sides slightly tapered and the underside slightly hollowed has been designed for use with poured joints. Holes are provided for pouring the joining material which flows into the cavities. In laying the brick a course is laid dry without mortar, and then the joints are filled by pouring the mortar into the holes. E.J.V.

Use of clay liners for intercepting sewer. Glenn E. Edgerton. *Brick Clay Rec.*, **82** [6], 201–202 (1933).—In constructing an intercepting sewer at the Lock and Dam No. 15 in the Mississippi River, 359,800 sq. ft. of vitrified clay sewerpipe liners were used for the double-barreled sewer. Illustrated. E.J.V.

Hollow tile or common brick *vs.* hollow tile and common brick. P. KUCHLER. *Tonind.-Ztg.*, **57** [39], 449–52; [42], 495–98; [44], 522–23 (1933).—Masonry is increasingly heat insulating the more porous it is. A complete review is given of many forms of hollow tile with dimensions, references, etc. W.M.C.

Closed-end hollow brick. FISKE BRICK & GRANULE CO. *Brick Clay Rec.*, **82** [6], 200 (1933).—A device has been developed for making a new type hollow, de-aired brick on an ordinary stiff-mud machine. Two rotating wheels set at the die mouth are so synchronized with the cutter that they squeeze the hollow column together at the point where the cutting wire passes through the clay column. Although these brick are 25% lighter than ordinary brick they can be produced at the same rate as solid brick. Illustrated. E.J.V.

Silos for forage conservation. L. MÜNSTERER. *Tonind.-Ztg.*, **57** [41], 487 (1933).—The main advantage of brick over concrete and steel silos is the greater protection obtained against freezing of the contents. W.M.C.

Rostone. DAVID E. ROSS. *Rock Prod.*, **36** [5], 44–46 (1933); for abstract see *Ceram. Abs.*, **12** [8], 298 (1933). W.W.M.

Overcoming sales resistance to brick pavements. IRVIN S. BADGER. *Clay-Worker*, **99** [6], 214 (1933).—At the 27th Annual Convention of the National Paving Brick Assn., B. gives reasonable answers to all objections made to brick pavements, showing how they can be used to overcome sales resistance. E.J.V.

Houses at A Century of Progress. ANON. *Brick Clay Rec.*, **82** [6], 198–99 (1933).—With new designs in houses making existing houses obsolete and with the Brick Mfrs.' Assn. reinforced brick masonry house occupying an advantageous location at the grounds, a new desire for modern homes is being created among the visitors. Illustrated. E.J.V.

A structural engineer "kibitzes" the brick industry. ANON. *Brick Clay Rec.*, **82** [6], 210–12 (1933).—Having had difficulty getting data from brick manufacturers on reinforced brick masonry, the author is impressed by the lack of interest among the manufacturers in this development in their field. E.J.V.

PATENTS

Method and apparatus for forming lugs on clay columns, etc. C. H. REKER (Metropolitan Paving Brick Co.). U. S. 1,914,981, June 20, 1933.

Building block and wall construction. D. D. WHITACRE. U. S. 1,915,111, June 20, 1933.

Refractories

Action of waste-wood ash on refractories. K. G. SKINNER AND N. L. FIELD. *Jour. Amer. Ceram. Soc.*, **16** [8], 393–403 (1933); see also *Ceram. Abs.*, **12** [3], 111 (1933).

Thermal expansion of refractories to 1800°C. R. A. HEINDL. Bur. Stand. *Jour. Research*, **10** [6], 715–35 (1933); R.P. 562.—The linear thermal expansions of the following 36 materials were measured: African chrome sand, Cuban, Grecian, friable African, Rhodesian Imperial, Indian, and Turkish chrome ores, Austrian, Californian, and electrically fused magnesites, a periclase brick, a spinel brick, two types of fireclay brick and two of fire clays, Kentucky, Tennessee, and English ball clays, Georgia kaolin and English china clay, an 80% alumina brick, artificial corundum, diaspore, bauxite, five mullites (each of which was prepared from different raw materials), two zircon brick and a furnaced zirconium silicate, silicon carbide, a silica brick, and an insulating brick. Data are also given on artificial graphite which had been preheated several times to 1800°C. Measurements were made using the specimen throughout the following cycle: (1) room temperature to 1000°C in an oxidizing atmosphere, (2) room temperature to some temperature above 1000°C but not exceeding 1800°C in a reducing atmosphere, (3) room temperature to 1000°C in an oxidizing atmosphere, and (4) room temperature to some temperature above 1000°C but not exceeding 1800°C in a reducing atmosphere. This procedure gave information relative to the effect on the expansion of the materials when tested in an oxidizing or reducing atmosphere, and when heated at a temperature higher than that which they received preliminary to the first test. Petrographic analyses give information relative to the constituents of the materials before and after the several heat treatments. The following facts were noted: (1) No apparent differences in expansion were obtained from room temperature to 1000°C when the materials were tested in either a reducing or oxidizing atmosphere except in the case of the chrome ores which showed an exceptionally high expansion between 700 and 1000°C under reducing

conditions. (2) The magnesites showed the greatest total expansion of the materials which had nearly a uniform rate of expansion. (3) The expansion curves of the zircons in the second tests showed greater irregularities above 950°C than the curves of the other materials. This was probably due to the decomposition of zirconium silicate into zirconium oxide and glass. (4) All materials showed some changes in total expansion in the second test when compared with those obtained in the first test although in some instances the difference was small. (5) Nearly all of the materials decreased in weight and length during the tests. The loss in weight was due to the volatilization of one or more of the constituents. Such volatilized material condensed in the upper tube of the set-up. In most cases this material was silica. Crystalline growths appeared on some of the specimens. At the end of the tests all chrome ores were covered with beads of metal, probably an alloy of iron and chromium. The reducing atmosphere was due to the oxidation of the graphite cylinder which was the heating unit. No gases were discharged into the furnaces. It was probable that the furnace gases were not strongly reducing below 600°C. R.A.H.

Refractory materials and the gas industry. A progress report. A. T. GREEN. *Gas World*, **98**, 441 (1933).—The report discusses (1) notes on the standard specifications, (2) arrested reactions and after-contraction, (3) mechanical strength at high temperatures, (4) thermal properties, (5) texture, porosity, and permeability, (6) silica products, (7) effect of repeated firings on the structure and properties of lime-bonded silica brick, (8) durability of refractories in gasworks, (9) flaking, and (10) deposition of carbon in gas producers. (*T.C.S.E.*)

Permeability of refractory materials to gases. F. H. CLEWS AND A. T. GREEN. Presented at meeting of English Ceramic Society, May, 1933; abstracted in *Colliery Guard.*, **146** [3778], 191 (1933); see also *Ceram. Abs.*, **12** [3], 111, 112 (1933). E.J.V.

Production of tridymite brick. II. HERMANN SALMANG AND BENNO WENTZ. *Ber. deut. keram. Ges.*, **14** [4], 141–55 (1933).—In making silica brick with an addition of 1.5% Na_2O and 1.5% Fe_2O_3 the transition to tridymite can be obtained at about 1250°. At 1050° a silica brick with a specific gravity of 2.45 can be obtained. On lowering the alkali content to 0.3% a complete quartz inversion is obtained. With 0.1% Na_2O the quartz is still only locally transformed. With the addition of alkali alone, without iron oxide or something similar, it is possible to obtain a transition which lacks a sufficient solidity. This solidity is not obtained even with the lime content increased to 7%. It is only possible when quartzite is used with an appropriate flux content. The "red spots" increase with increasing lime content. Phosphoric acid and boric acid hinder the quartz inversion in every form. This is often aided by the pyrochemical bases which neutralize the acids. Inoculation experiments on silica mixes with tridymite or cristobalite meal gave no positive results. The concentration of alkalis on the surfaces of the molded articles is prevented by using them in an insoluble form. Na_2SiF_6 is not well suited for this. The best is a frit of $1Na_2O$, $1Fe_2O_3$, and $3SiO_2$ melted under reducing conditions. This is added in a finely powdered state and produces an excellent inversion. Thermal expansion curves show a sharp jump for cristobalite brick at 230°. Tridymite brick have a proportionately uniform expansion curve. The inversion of tridymite was noted at 100 ± 7° and 141 ± 7°. The total thermal expansion is dependent to a great extent on the proportion of glassy material which increases with higher firing temperature, longer firing time, and increasing amount of flux. For Part I see *Ceram. Abs.*, **10** [6], 437 (1931). E.J.V.

Silica as a refractory material. III. C. N. WITHEROW. *Brick Clay Rec.*, **82** [6], 208–209 (1933).—The quartzites furnish most of the raw material used in the manufacture of silica brick, silica cement, and ganister products; in a few cases hard well-bonded sandstones and chert are used to a limited extent. The physical and chemical properties of quartzites are discussed. The materials commonly used in silica cements are taken up. As adjuncts to silica refractories, W. takes up alumina-silica refractories and the sillimanite and mullite refractories. Efforts that have been made to improve silica refractories, such as increasing the tridymite content to decrease spalling, etc., are listed. For Part II see *Ceram. Abs.*, **12** [8], 299 (1933). E.J.V.

Silicon carbide, its production, and the manufacture of rods. L. NAWO. *Elektrowärme*, **3**, 82–84 (1933).—SiC is not attacked by O_2 up to 1000°; from 1350 to 1500° it is oxidized by O_2 to form fused SiO_2. Metal oxides are reduced by SiC, *e.g.*, CuO at 800°, Fe_2O_3 and Ni oxide at 1300°, Mn oxide at 1360°, and Cr oxide at 1370°. Acids do not attack SiC, but it reacts with alkalis. Cl acts upon it at 600° superficially but at 1200° completely. The manufacture of heating elements, especially the proper preparation of the ends for electric connection, and arrangements for water cooling are described and illustrated. (*C.A.*)

Selecting the right chrome ore. II. A. DE MACEDO. *Blast Fur. Steel Plant*, **21** [6], 335–36 (1933).—Petrographic studies of chrome ores show definitely that the physical structure of each ore has an important bearing as to its suitability for refractory applications. A study of a thin section will permit the determination of the suitability of the ores where formerly only chemical analysis was used. For Part I see *Ceram. Abs.*, **12** [8], 299 (1933). E.J.V.

True cost of raw materials to the firebrick manufacturer. W. BOYD MITCHELL. Presented at meeting of English Ceramic Society, May, 1933; abstracted in *Colliery Guard.*, **146** [3778], 191 (1933). E.J.V.

Weathering of brick. A. W. RICK. *Korrosion und Metallschutz*, **9** [1], 10 (1933).—The factors causing the decomposition of brick are briefly reviewed. J.B.A.

Experiments on fire clay. M. REITZ. *Keram. Rund.*, **41**, 124 (1933).—The fired body of fireclay ware should have a water absorption not exceeding 10%. Experiments were conducted on casting of fireclay ware. The preparation of a suitable slip depends upon the raw materials used. A slip containing only 22.5% of water was prepared by allowing a fireclay body to age for three days, then passing it through a pug four times, and finally allowing it to weather for 14 days in a fairly dark place. Electrolytes and water were then added. The body was a coarse grog body containing 25% plastic clay, 20% kaolin, 10% feldspar, and 45% grog. To 100 kg. (dry weight) of this body were added 65 g. soda, 42 g. soda lye, and 28 g. tannin. Large, thick baths were successfully cast; the drying shrinkage was 3.5%, and the firing shrinkage (cone 9) 3.3%. The results of a number of such experiments indicate that a casting body must first undergo wet preparation; the longer the body is aged, the less water and electrolyte are required. Notes are given on the casting process, the engobe glaze, and firing. (*T.C.S.E.*)

Aluminium industry. GEORGE BOEX. *Chem. Trade Jour.*, **92** [2403], 455–56 (1933).—A detailed account is given of the Bayer process of bauxite treatment used by the British Aluminium Company. M.V.K.

Bavarian graphite. ANON. *Tonind.-Ztg.*, **57** [42], 499–500 (1933).—This type of graphite shows comparatively small flakes, but satisfactory refractoriness and thermal conductivity. By flotation and grinding of the raw materials the carbon content is increased to 98%. No free impurities are present. W.M.C.

Manufacturing sintered dolomite in shaft and rotary kilns. C. KJEHLSEN. *Tonind.-Ztg.*, **57** [45–46], 533–34 (1933).—The most satisfactory scheme is a combination of shaft and rotary kilns, shaft kilns being used for large-sized raw materials and rotary kilns for the fine particles. Details are given for operating both types of furnaces, the output ranging around 160 tons. Recovery of the waste heat of the clinkers is emphasized. W.M.C.

Refractory material for cement rotary kilns. J. FAUNER. *Cement*, **6**, 113–23 (1933). (*B.C.A.*)

Tercod—a new refractory brick for electric furnaces. G. S. DIAMOND. *Trans. Electrochem. Soc.* (Preprint), **63**, 4 pp. (1933).—An improved silicon carbide refractory brick has been developed. The thermal expansion is exceptionally low, being only $^1/_9$ that of silica brick. The electric and thermal conductivities are much higher than those of SiO_2 refractories. The C bond gives rigidity up to the dissociation temperature of SiC. Tercod is inert to acid or neutral slags but is attacked by basic slags. The borosilicate glazed brick is applicable to furnaces melting irons with 3% C or above and melting nonferrous metals. Experiments have been made with fused alumina glazes; brick thus faced have been successfully used in melting low-C steels and Ni. (*C.A.*)

Refractory materials and kiln construction. W. G. LINGBEEK. *Arch. Suikerind.*, **40**, 717–19 (1932); see also *Ceram. Abs.*, **12** [8], 300 (1933). (*C.A.*)

Repairs to steel furnaces. WALTER LISTER. *Metallurgia*, **8** [44], 53–54 (1933).—The service from steel furnaces depends on the treatment to which they are subjected, but the method of carrying out necessary repairs has an important influence. Repairs to basic furnaces are discussed in detail, including (1) the basic brick bottom, and (2) the use of hand and pneumatic ramming. There are only two materials in general use for making a basic hearth, *e.g.*, dolomite and magnesite. M.V.K.

Spalling of fire brick. ANON. *Chem. Trade Jour.*, **92** [2404], 481 (1933).—To minimize the risk of spalling, the following points are of importance: (1) lighting up with coal fires; wood and oily waste give too much flame for the surface of the cold brickwork; (2) the slowest practicable heating and cooling of the brick under 800°C; (3) use of brick of standard sizes in place of large special shapes and of shapes with severe changes in mass and section; and (4) adoption of special quality brick where fast heating and/or cooling can not be avoided. M.V.K.

Regenerators for open-hearth furnaces. H. TRINIUS. *Arch. Eisenhüttenwesen*,

6 [6], 231–39 (1932); *Iron Coal Trades Rev.*, **126** [3385], 51 (1933); abstracted from a communication from the German Heat Economy Bureau at Düsseldorf; for abstract see *Ceram. Abs.*, **12** [8], 300 (1933). W.E.R.

Refractory jointing cements. A. T. GREEN, F. WHEELER, AND H. BOOTH. *Feuerfest*, **9** [1], 7 (1933); for abstract see *Ceram. Abs.*, **11** [9], 493 (1932). M.V.K.

Plibrico observation port. PLIBRICO JOINTLESS FIREBRICK CO. *Brick Clay Rec.*, **82** [6], 214 (1933).—This inexpensive but efficient observation port is provided with a divided cover which opens at a touch on the handle and closes automatically the moment the handle is released by the operator. The overlapping sections of the cover close tight, practically eliminating any infiltration of excess air. E.J.V.

Progress in the refractory field in the United States in 1932. I. W. STEGER. *Feuerfest*, **9** [5], 68–71 (1933).—S. discusses the latest investigations in the refractory field according to the *Journal of the American Ceramic Society*. References are given. M.V.K.

Refractories: a review of 1932. ANON. *Times Eng. Supp.*; abstracted in *Refrac. Jour.*, **9** [3], 96–97 (1933).—This is the first part of a review of developments in refractories in 1932. It takes up machine-made fire brick, silica brick, and alumina and magnesite brick. W.W.M.

BOOK

Manufacture of Grog Brick. P. P. BUDNIKOFF AND R. L. PEWSNER. Gosstrojisdat, Moscow and Leningrad, 1932. 1.85 R. Reviewed in *Feuerfest*, **9** [5], 79 (1933).—This book describes the latest achievements in the field of the production of grog brick in Europe and the U. S. It comprises (1) characteristics, (2) obtainment, (3) control and properties of raw materials, (4) firing and grinding of grog, (5) preparation of the mix, (6) molding and shaping, (7) drying and firing the products, and (8) the firing of the furnace. Estimation of quality and standard specifications of grog brick are given also. M.V.K.

PATENTS

Heat insulator. J. B. BARNITT AND R. B. DERR (Aluminum Co. of America). U. S. 1,870,437, Aug. 9, 1932. A heat insulator comprises aluminum oxide and a bonding agent, the oxide having been artificially produced in a finely divided, substantially monohydrate form from aluminous material of higher hydration.

Process of producing pure aluminium combinations adapted for the production of aluminum. MAX BUCHNER. U. S. 1,914,768, June 20, 1933. In the process of producing aluminium fluoride and double compounds of aluminium, the steps comprise producing a basic aluminium nitrate solution by treating a fluorine free raw material containing alumina with a quantity of nitric acid insufficient to completely form $Al(NO_3)_3$ with the alumina present and adding an alkali fluoride to the resulting basic aluminium nitrate solution.

Suspension-wall bracket. T. E. MCGRAIL. U. S. 1,914,974, June 20, 1933.

Recuperative soaking-pit furnace. M. H. MAWHINNEY (Electric Furnace Co.). U. S. 1,915,470, June 27, 1933.

High-temperature cement. P. S. DENNING (F. E. Schundler). U. S. 1,916,971, July 4, 1933. A high-temperature cement capable when set of withstanding high temperature without splitting or spalling includes the following initial ingredients: a water solution of magnesium sulfate, a citrate radical to the amount of $^1/_2$ of 1% of the weight of the magnesium sulfate, magnesium oxide, and an aggregate to the amount of substantially $^1/_3$ of the mass by weight, the aggregate comprising a quantity of particles of exfoliated vermiculite.

Refractory lining. E. F. NORTHRUP (Ajax Electrothermic Corp.). U. S. 1,917,849, July 11, 1933.

Sintered magnesia and refractory materials containing sintered magnesia. ALTERRA AKT.-GES. Brit. 394,115, June 28, 1933.

Joint between a metal and a siliceous refractory material. J. E. LILIENFELD. Brit. 394,311, July 5, 1933.

Refractory compositions. ULRICH HAHN. Ger. 572,019, Dec. 2, 1930. As a binder in refractory compositions, use is made of a mixture of an albumin with one or more alkaline earth metal oxides. Other alkalis or alkaline salts, with or without water, may be added to the mixture. (*C.A.*)

Furnace walls, etc. DIDIER-WERKE A.-G. Ger. 573,014, April 8, 1931. The mortar expressed when the brick are pressed together is allowed to remain on the inner face of the wall. The mortar used may comprise a refractory substance, *e.g.*, SiC,

ZrO_2, or corundum, and a small amount of a substance promoting the hardening of the mortar, *e.g.*, water-glass or sulfite cellulose lye. (*C.A.*)

Compositions for making crucibles or lining metallurgical furnaces. FELIX SINGER. Ger. 573,030, March 21, 1928. Use is made of compositions containing BaO 31 to 51, Al_2O_3 17 to 37, and SiO_2 22 to 42%. Part or all of the BaO may be replaced by an equimolecular amount of SrO. The compositions are not corroded by fused Al or Al alloys. (*C.A.*)

Alumina. YÔSEI SUZUKI AND KAN TANAKA (Rikagaku Kenkyûzyo). Japan. 94,254, Jan. 21, 1932. By heating a mixture of clay or bauxite containing Ti, C, and Fe (or Fe_2O_3) and sulfide of Al, Na, K, or Mg in an electric furnace, a mixture of Al_2O_3 and ferrosilicon is obtained, and most of the Ti is driven off as TiS_2. The Al_2O_3 contains only a small amount of SiO_2, TiO_2, and Fe_2O_3. (*C.A.*)

Terra Cotta

Salts causing crawling of glazes. ANON. *Tonind.-Ztg.*, **57** [47], 544 (1933).—Glazed face brick have been studied which show a partial crawling of the glaze applied. Efflorescence was observed on some green tile. These tile were found later to show the crawling of the glaze. The salts enter the tile during drying from a slag layer inside the drying shed. W.M.C.

PATENT

Machine for making roofing tile, etc. O. WALTER. Brit. 393,856, June 21, 1933.

Alkali- and acid-proof stoneware. B. FROSTERUS AND C. G. HÖGMAN (invented by B. Frosterus). Swed. 71,037, Jan. 27, 1931. Finely ground silicate rock rich in $MgCO_3$, *e.g.*, talc-magnesite slate, from which magnetic substances may be separated, is mixed with a binder and, if necessary, with another finely pulverized MgO-rich material such as Mg silicate, magnesite, or dolomite so as to obtain a mass with almost equal contents of MgO and SiO_2 or only slightly less of the former, after which the mass is formed into brick or stones and fired. (*C.A.*)

White Wares

Difficulties in firing decorated whiteware. J. T. ROBSON. *Jour. Amer. Ceram. Soc.*, **16** [8], 345–55 (1933).

Use of auxiliary fluxes in dinnerware bodies. G. A. LOOMIS. *Jour. Amer. Ceram. Soc.*, **16** [8], 356–59 (1933).

Resistance to sudden temperature change of some bodies of the system talc–clay–mullite. R. M. KING AND C. L. EVANS. *Jour. Amer. Ceram. Soc.*, **16** [8], 360–62 (1933).

"Calit" and "Calan," two new ceramic insulating materials. J. WALLICH. *Z. Ver. deut. Ing.*, **77** [18], 483 (1933).—These materials are chemically pure, iron-free magnesium silicates which, when fired at about 1400°C, result in dense masses. They make excellent insulating materials with small dielectric loss. L.T.B.

Stamping of porcelain insulators. A. E. RABINOVICH. *Keram. i Steklo*, **9** [3], 10–11 (1933).—On the basis of practical data, R. discusses the production of stamped electro-porcelain insulators. Compositions of porcelain mixes and of glazes for covering the insulators are given. M.V.K.

Ten years' progress in the whiteware industry. EDWARD SCHRAMM. *Ceram. Ind.*, **21** [1], 22–24 (1933).—S. cites new tests, methods, processes, and products to show the advance of the whiteware industry during the past ten years. W.W.M.

PATENTS

Insulator. W. D. KYLE (Line Material Co.). U. S. 1,914,436 and 1,914,437, June 20, 1933. S. D. SPRONG (Engineering Products Corp., Inc.). U. S. 1,915,838, June 27, 1933.

Bench for pottery molds. B. H. GREENE. U. S. 1,914,740, June 20, 1933.

Tile. T. E. MCCUTCHEON. U. S. 1,917,139, July 4, 1933.

Proceeding for firing in piles the articles of nonglazed porcelain especially suitable for cooling use. GIOVANNI FUSCHI AND MAURIZIO KORACH. U. S. 1,917,964, July 11, 1933.

Sink for kitchen cabinets. A. P. WOOLFOLK (Standard Sanitary Mfg. Co.). U. S. 1,918,074, July 11, 1933.

Washdown closets. F. B. THORPE. Brit. 393,751, June 21, 1933.

Equipment and Apparatus

Design, construction, and costs of arc-welded pebble mills. D. L. PELLETT. *Paper Trade Jour.*, **95** [25], 27–30 (1932).—Large pebble mills with cast heads and riveted steel shells are usually built. The cast head is bolted to an adapter ring which is riveted to the shell plate. This type of construction is excessively heavy and necessitates the use of large and expensive patterns and drill jigs. P. describes an all-steel welded construction which is lighter and much cheaper to construct. On mills 10 ft. long and 7 ft. 6 in. in diameter the welded mill weighs 11,000 lb. less than the cast one. The manufacturing cost for the cast one is $1220.00 as compared with $516.00 for the welded mill. Furthermore, the builder of the old mill needs 50% profit to cover his large plant, expensive equipment, and risks of defective castings as compared with the 30% profit required for the arc welding builder with his smaller plant, inexpensive equipment, and lack of risk. The design, stress analysis, and manufacturing costs are discussed and illustrated by diagrams and photographs. The outer shell is a plate $^1/_2$ in. thick, rolled into a cylinder and butt welded together. The head is a circular steel plate with a steel casting welded to the plate at its center. The casting is bored at the driven end for the drive shaft which is welded in place. Twelve radial ribs $^3/_4$ in. thick resist the bending moment imposed on the head by the vertical reaction at the bearing. Considering the head plate as having no strength, since its inside surface is subject to corrosion, and taking the working stress in the ribs as 8000 lb./sq. in., a factor of safety of about 4 is obtained. Strength of welds is based on data published by the Westinghouse Electric and Mfg. Co. Welds in tension, compression, or bending were stressed at 5000 lb./sq. in., and welds in sheer at 4000 lb./sq. in. J.L.G.

Krupp tube mill with air separation and drying system. ANON. *Tonind.-Ztg.*, **55** [82], 1147–49 (1931); abstracted in *Mech. Eng.*, **55** [2], 130 (1933). F.G.H.

Drying clay products. W. D. RICHARDSON. *Clay-Worker*, **99** [6], 212–13 (1933).—R. discusses recent articles on drying and driers by Garve, Lovejoy, and Keplinger and attempts to show in his review and analysis where debatable statements in them can be corrected. Several forms of driers are discussed and improvements are pointed out. E.J.V.

Direct gas heat under control reduces drying time. FERGUSON. *Ceram. Ind.*, **20** [6], 279 (1933).—A gas heat drier at the plant of the Star Porcelain Co., which reduces the drying time from 2 weeks to 22 hours, is described. W.W.M.

Waste heat for drying common brick. P. THOR. *Tonind.-Ztg.*, **57** [42], 494–95 (1933).—This is a discussion of the paper by Leder (*Ceram. Abs.*, **11** [7], 424 (1932); **12** [3], 107 (1933)). New data are presented for the efficiency of drying installations. W.M.C.

Proposed American standard for sieves. LEWIS V. JUDSON. *Metal Cleaning & Finishing*, **5** [6], 262 (1933).—Work on formulation of an international standard for testing sieves is being carried on with committees working on the following subjects: coarse sieves, fine sieves, pigments, representation of data, and calibration. This is a progress report as more work is necessary before the standard is complete. See also *Ceram. Abs.*, **11** [11], 547 (1932). E.J.V.

Sieve limitations and the fineness modulus. A. HUMMEL. *Zement*, **21** [48], 671–75 (1932); abstracted in *Rock Prod.*, **36** [2], 50–51 (1933).—The grading of aggregates might follow some ideal curve such as the Fuller, a similar curve, a specification of maximum and minimum amounts passing different screens, or the fineness modulus. Investigations made in Germany and the U. S. show that many gradings outside the usual continuous grading specifications give satisfactory strength, density, and workability, so that care must be exercised in establishing sieving limits. The fineness modulus may have a more general usefulness in drawing up specifications for concrete aggregates. M.V.K.

Smoke-density scales. H. E. BUMGARDNER. *Mech. Eng.*, **55** [3], 200 (1933). F.G.H.

Color changes of hygroscopic metallic salts and their use as hygrometers. ALFRED SCHWARTZ. *Messtechnik*, **9** [5], 87–92 (1933).—Experiments on the behavior of hygroscopic metallic salts in varying degrees of humidity are described. New methods of clearly determining the color changes of such materials are discussed. A hygrometer

constructed on the basis of color changes of such salts is described and comparisons are made on similar measurements with it and a known capillary hygrometer. Illustrated. E.J.V.

Preparing raw materials for roofing tile. E. HÜTTEMANN. *Tonind.-Ztg.*, **57** [45–46], 530–32; [48], 557–58 (1933).—Machines which are being used in clay pits and machines for separating or mixing different clay layers are described. Pulverizing and drying the clay should be carried out before aging. The most important machines used in disintegrating the raw materials are briefly described. See also *Ceram. Abs.*, **12** [5], 196 (1933). W.M.C.

Testing of sifting cloth. H. HECHT. *Tonind.-Ztg.*, **57** [41], 483–86 (1933).—Methods are described for testing standardized sifting cloths. Special micrometer screws have been devised as well as optical methods. Pictures are shown of satisfactory and nonsatisfactory samples. The method of the Tonindustrie Laboratory is being used on a large scale. W.M.C.

Influence of voltage on semiconductors. W. HÜTER. *Arch. Electrotech.*, **27** [5], 341–46 (1933).—Conductors containing silicon carbide show a change of electric resistance according to the voltage applied. The change of resistance is not uniform. W.M.C.

Simple apparatus for photographic registering of precipitation curves in sedimentation analyses. H. STAMMREICH. *Ber. deut. keram. Ges.*, **14** [2], 84–87 (1933).—The "Sedigraph" is used for making sedimentation analyses and a simple photographic registering apparatus has been devised for recording the precipitation curves. Illustrated. E.J.V.

Steele clay conditioning (de-airing) equipment. ANON. *Clay-Worker*, **99** [6], 213 (1933).—Construction and operation details are given. E.J.V.

Pressure and suction fans. JOHN W. ROMIG. *Glass Ind.*, **14** [7], 75–77 (1933).—Fans may be used for exhausting or suction, or for blowing or pressure. Some of the computations in connection with the use of fans are discussed in detail. Laws which exist in fan operation are as follows: (1) the capacity of a given fan varies directly with the speed, (2) the pressure varies as the square of the speed; (3) the horsepower input varies as the cube of the speed, and (4) horsepower and pressure vary directly as the barometric pressure and inversely as the absolute temperature. Care in selection of fans for particular service requirements is emphasized. See also *Ceram. Abs.*, **12** [6], 236 (1933). E.J.V.

Orifices for the measurement of flow. HANS EULER. *Arch. Eisenhüttenwesen*, **5** [5], 231–49 (1931); **6** [3], 95–104 (1932); *Iron Coal Trades Rev.*, **126** [3385], 45 (1933); abstracted from Communications No. 156 and 157 from the German Heat Economy Bureau at Düsseldorf. W.E.R.

Rolled steel in machine construction: advantages over cast iron. H. G. MARSH. Paper read before Amer. Iron and Steel Inst., May 25, 1933; abstracted in *Iron Coal Trades Rev.*, **126** [3406], 892 (1933). W.E.R.

Winning and transporting of basic raw materials used in the heavy clay and refractories industries. F. WEST. Presented at meeting of English Ceramic Society, May, 1933; abstracted in *Colliery Guard.*, **146** [3778], 191 (1933). E.J.V.

Winning and transport of clay. E. GWYNNE VEVERS. Presented at meeting of English Ceramic Society, May, 1933; abstracted in *Colliery Guard.*, **146** [3778], 191 (1933). E.J.V.

Vacuum furnace design. K. K. KELLEY. *Ind. Eng. Chem., Anal. Ed.*, **4**, 391 (1932).—The furnace contains a copper block of 22 kg. heated by a coil of nichrome ribbon of 8 ohms resistance and surrounded by Monel metal radiation shields which protect the vacuum joints. The jacket is of two cylindrical steel shells, and all leads are taken out through Pyrex glass tubes sealed with de Khotinsky cement. At 1000° a pressure of 0.1 mm. can be maintained after a preliminary "out-gassing" of the copper block. (*J.S.G.T.*)

Ancient laboratory apparatus. ANON. *Laboratory*, **6** [1], 3–5 (1933).—Ancient laboratory glassware, reverberatory furnaces, muffles, and beehive ovens are described and illustrated. F.G.H.

BOOKS AND BULLETIN

Science and Practice of Drying. ARTHUR E. BROWN. British Clayworker, 43 Essex St., Strand, London, W.C. 2, England. Price 7s 9d. *Brick Clay Rec.*, **82** [6], 204 (1933).—This scientific and practical treatise is written under the following headings: air as a carrier of heat, characteristics of clay, practice of drying, modern humidity chamber drier, tunnel driers, and practical drying of clay. E.J.V.

Modern Materials Handling. S. J. KOSHKIN. *Mech. Eng.*, **55** [2], 143 (1933); for abstract see *Ceram. Abs.*, **11** [12], 628 (1932). F.G.H.

Methods for servicing noble metal thermocouples. R. S. BRADLEY. *Amer. Refrac. Inst. Tech. Bull.*, No. 39, 6 pp. (1933).—The need for maintenance of thermocouples used in kilns is described. Those used in tunnel kilns need more frequent attention than do those in periodic kilns because of the continuity of service of the former. Methods and apparatus are described whereby the four operations, (1) testing for homogeneity, (2) welding, (3) annealing, and (4) calibration, can be conveniently completed at the plant of the user. W.E.R.

PATENTS

Brick-cleaning machine. G. G. NOBLE AND O. P. QUIGLEY. U. S. 1,915,751, June 27, 1933.

Magnetic separators for minerals, etc. W. W. TRIGGS (Exolon Co.). Brit. 392,532, May 31, 1933.

Apparatus for sifting potters' slip and for analogous purposes. A. JONES AND W. H. JONES. Brit. 394,057, June 28, 1933.

Kilns, Furnaces, Fuels, and Combustion

Fundamentals and economies in the clay industries. XXVIII. ELLIS LOVEJOY. *Clay-Worker*, 99 [6], 208–209 (1933).—In continuation of his discussion of kilns, L. explains the differences in, advantages and disadvantages of, and operating principles of forced and induced draft. The position of the stack for the different types of kilns is also treated thoroughly. For Part XXVII see *Ceram. Abs.*, **12** [8], 307 (1933). E.J.V.

Forced-air circulation furnaces. ANON. *Metal Ind.* [London], **42** [24], 617–18 (1933).—Rapidity of heating in the new forced-air circulation furnace is obtained by means of a patented centrifugal fan. The heat absorbed by the air from the elements is given up to the charge. The high pressure obtainable by using the centrifugal fan permits a powerful circulation which is continuous. No fresh air is drawn into the chamber and no hot air is lost. The heavy insulation makes heat losses negligible and results in low power consumption. M.V.K.

Changing a periodic furnace into a continuous kiln for firing face brick. L. SCHIELE. *Tonind.-Ztg.*, **57** [44], 521–22 (1933).—Five periodic kilns with three added chambers have been combined to form a continuously operated kiln. Illustrated. W.M.C.

Construction of tunnel kilns. N. NORKIN. *Keram. i Steklo*, **9** [3], 13–16 (1933).—A detailed account of different types of tunnel kilns is given. See also *Ceram. Abs.*, **11** [8], 465 (1932). M.V.K.

Muffle kiln of high efficiency. F. H. NORTON AND J. V. DUPLIN, JR. *Can. Chem. Met.*, **17** [5], 104 (1933); see also *Ceram. Abs.*, **12** [4], 168 (1933). E.J.V.

Grid pulverized-fuel burner. T. F. HURLEY. Dept. of Sci. & Ind. Research, Fuel Research Board, *Tech. Paper*, No. 36; abstracted in *Iron Coal Trades Rev.*, **126** [3406], 891–92 (1933). W.E.R.

Chemistry of gaseous fuels used for glass, enamel, and pottery. II. JOHN W. ROMIG. *Ceram. Ind.*, **20** [6], 274 (1933).—R. discusses the properties of producer gas, natural gas, blue water gas, carburetted gas, and oil-still gas. The best fuel depends upon the type and condition of flame desired. The formula for determining theoretical flame temperature is given. Some graphic data are presented. For Part I see *Ceram. Abs.*, **12** [8], 307 (1933). W.W.M.

Burning problem of gases. ANON. *Laboratory*, **6** [2], 22–24 (1933).—The design and construction of Bunsen burners and high-temperature burners for rapid and slow burning gases are described and illustrated. F.G.H.

Gaseous fuels for industrial purposes. A. E. BLAKE. *Iron Age;* abstracted in *Iron Coal Trades Rev.*, **126** [3408], 966 (1933). W.E.R.

Evaluation of gas coals. P. SCHLÄPFER. *Monats-Bull. Schweiz. Ver. Gas- u. Wasserfachmännern*, No. 6, 18 pp. (1932).—The importance of the ash content of a gas coal is emphasized, and attention is drawn to the relationship between the volatile matter and ash in the coal to the ash in the coke. While the proximate analysis is valuable for purposes of control, other tests are often necessary, particularly with new coals or coal blends; these tests include determinations of caking power, swelling, and swelling pressure. For the production of coke of uniform quality it is desirable that the banded constituents should be well distributed. A more complete examination would also in-

clude a distillation test, determination of the calorific value, and the ultimate analysis. The swelling properties of a coal are greatly reduced by preheating. Though the presence of O_2 hastens this change, it occurs also if the coal is heated in an inert gas or *in vacuo*. Similarly, the swelling properties are influenced by the rate of carbonization. (*B.C.A.*)

Brands of coal used in the brick industry. W. GRESSLER. *Tonind.-Ztg.*, **57** [45–46], 534–35 (1933).—Figures are given for the amount of soft and hard coal used in pressing and firing common brick. The quality and heating value of the coal should be kept as uniform as possible in order to secure uniformity of the brick. W.M.C.

Constitution of coal. F. V. TIDESWELL. Presented at meeting of English Ceramic Society, May, 1933; abstracted in *Colliery Guard.*, **146** [3778], 191 (1933). E.J.V.

Relative fuel economy of electricity, gas, oil, and solid fuel as heating agents. A. H. BARKER. Preprint of the Institution of Electrical Engineers, London; abstracted in *Mech. Eng.*, **55** [2], 121 (1933); for abstract see *Ceram. Abs.*, **12** [4], 174 (1933). F.G.H.

Combined coal drying and grinding plants for the cement industry. W. JAEDEL. *Tonind.-Ztg.*, **57** [43], 508–10 (1933). W.M.C.

Marketing of pulverized coal in Great Britain. H. D. TOLLEMACHE. *Steam Engineer*, **2** [3], 131–33 (1932); abstracted in *Mech. Eng.*, **55** [2], 121–22 (1933). F.G.H.

Large pressure tanks for oil-gas storage. L. S. STILES. *Mech. Eng.*, **55** [3], 162 (1933). F.G.H.

BOOK AND BULLETIN

Heat Transmission. WILLIAM H. MCADAMS. McGraw-Hill Book Co., N. Y., 1933. 383 pp. $5.00. *Jour. West. Soc. Eng.*, **38** [3], 182 (1933); see also *Ceram. Abs.*, **12** [8], 307 (1933). W.W.M.

Flotation processes for cleaning fine coal. H. F. YANCEY AND J. A. TAYLOR. Bur. Mines *Information Circ.*, No. 6714. 31 pp. Free. The report describes and compares froth-flotation and Trent processes. Patents pertaining to coal flotation are listed. R.A.H.

PATENTS

Kiln. H. C. KLEYMEYER. U. S. 1,913,599, June 13, 1933. In a kiln a firing chamber has a floor with openings therein, a wall around the floor, an arcuate dome on the wall, and means associated with the wall for delivering heat equally to all parts of the dome adjacent the wall, the means comprising a flash wall and spaced blocks between the walls.

Apparatus for feeding pulverized fuel. HARLOWE HARDINGE (Hardinge Co., Inc.). U. S. 1,914,828, June 20, 1933.

Tunnel kiln. P. H. DRESSLER (Swindell-Dressler Corp.). U. S. 1,916,363, July 4, 1933.

Ceramic ware treating method and apparatus. C. L. COLBERT (Fiske & Co., Inc.). U. S. 1,917,924, July 11, 1933. Ware is treated in a tunnel kiln having a preheating zone, a firing zone, and a cooling zone, a flashing zone and a tempering zone disposed between the combustion zone and the cooling zone, the flashing zone being provided with inlets to supply surface coating material at high temperature and outlets arranged to coöperate with the inlets in causing the circulation of the coating material in contact with the surface of the ware, and means to supply a relatively large quantity of cool air to the tempering zone to effect a rapid cooling of the ware emerging from the flashing zone, thereby to set the finish imparted to the ware by the flashing treatment.

Tunnel kilns. J. WEDGWOOD & SONS, LTD., AND N. WILSON. Brit. 392,839, May 31, 1933.

Firing brick and tile in annular furnaces. A. JÖNSSON. Swed. 70,997, Jan. 20, 1931. Mechanical features of furnace and operation are described. (*C.A.*)

Geology

Cyanite deposits of North Carolina. JASPER L. STUCKEY. *Econ. Geol.*, **27** [7], 661–74 (1932).—The most important of the widely distributed cyanite deposits in the Piedmont Plateau and Appalachian Mountain sections of N. C. are found in a belt 6 to 8 miles wide extending along the line of the Black and Great Craggy mountains from the vicinity of Burnsville, Yancey County, to Swannanoa, Buncombe County. All of the investigated occurrences of cyanite in N. C. are found in highly metamorphosed

acid rocks or in pegmatite dikes and quartz veins inclosed in such rocks. S. discusses representative types from three localities. These types fall into two general groups, (1) disseminated deposits forming irregular lenses in schistose rocks, and (2) pocket or bunchy deposits occurring as lenses in pegmatite dikes or quartz veins. Disseminated deposits are widely distributed in acid metamorphic rocks of Archean, Algonkian, and Cambrian age while the pocket or bunchy deposits are confined to quartz veins and associated pegmatite dikes occurring in rocks of the same age. The cyanite crystals found vary in color from light blue through gray to white and colorless and in size from a fraction of an inch to 3 or 4 in. long. S. presents evidence to show that the cyanite deposits have been formed by replacement of acid crystalline rocks, pegmatite dikes, and quartz veins. He decides that the evidence indicates these deposits as belonging to the Carboniferous age. No commercial production of concentrated cyanite is carried on at present in North Carolina but one test plant has been built near Burnsville, Yancey County, and is carrying on concentration tests. Pockets or bunchy lenses are too small and widely scattered to invite profitable mining. Disseminated deposits average about 20% cyanite. Fine grinding is necessary to produce a clean product owing to the close association of cyanite with quartz, garnet, and mica. Practical tests indicate a recovery of 11 to 14% pure cyanite. All available information indicates a large supply of cyanite in disseminated deposits. Illustrated with a map and photomicrographs.
J.L.G.

Occurrence of andalusite and related minerals at White Mountain, California. P. F. KERR. *Econ. Geol.*, **27** [7], 614–43 (1932).—The andalusite mine near White Mountain, Calif., contains all of the commercial ore known at present in the U. S. This is included in nine claims owned by Champion Sillimanite, Inc. These claims range from 7500 to 10,000 ft. above sea level along the face of a cliff on the west side of White Mountain. Another claim one mile down the canyon, owned by Moreau, is now being developed. Nearly all of the andalusite mined has been used by the Champion Spark Plug Co. in the manufacture of spark plugs. A few small lots have been sold at $100 per ton. Andalusite imparts unusual strength and resistance to heat shock to porcelains in which it is used and is therefore valuable in spark plug manufacture. The andalusite at White Mountain occurs in irregular segregations in a huge lenticular quartz mass which has recently been considered to be of sedimentary origin. A narrow schist of sericite occurs on either side of the quartz mass but these schists contain no andalusite. The minerals commonly associated with the andalusite are corundum, quartz, muscovite, pyrophyllite, diaspore, alunite, rutile, and lazulite. The mixture is such that a typical chemical analysis representing a carload lot recalculated on an $Al_2O_3 \cdot SiO_2$ basis may run over 90% $Al_2O_3 \cdot SiO_2$. Therefore, it is not necessary to separate such constituents from the commercial andalusite before shipment. The ore is hand sorted at the mine and then carried to the shipping point at Shealy by mule. Here it is mixed to insure an even blend of andalusite. Quality is estimated by means of specific gravity. Control is given by the use of Jolly balances to maintain a specific gravity of 3.01 to 3.06. K. gives a separate description of each of the most significant minerals of the deposit and discusses the relationship of these minerals to each other in following the processes occurring in the formation of the andalusite mass. Petrographic and X-ray diffraction studies of these minerals were made and the results are included in the paper. Illustrated with photographs, sketches, X-ray diffraction patterns, and photomicrographs.
J.L.G.

Witherite and its application. HENRY LOUIS. *Chem. Trade Jour.*, **92** [2404], 478–79 (1933).—Witherite, the native carbonate of baryta, contains up to 77.6% baryta and is readily soluble in dilute acids. It crystallizes in the orthorhombic system, being nearly isomorphous. Its hardness is from 3 to 3.75 on Mohs' scale, and its specific gravity ranges from 4.29 to 4.35. Witherite occasionally occurs in good crystalline masses which are very transparent; it is easily fusible and colors the blowpipe flame the green color characteristic of barium. Witherite is used for a large number of purposes; its chief demand is that of a mineral from which all other barium compounds can readily be produced. In the native state it is used to prevent efflorescence in brick manufacture.
M.V.K.

Potash development in southeastern New Mexico. H. I. SMITH. *Glass Ind.*, **14** [7], 85 (1933).—The recently developed potash industry in southeastern N. M. marks the latest and perhaps culminating effort to obtain a domestic source of potash.
E.J.V.

Contribution of clay and organic matter to the base-exchange capacity of soils. RICE WILLIAMS. *Jour. Agric. Sci.*, **22**, 845–51 (1932).—W. defines base-exchange capacity as the maximum possible content of exchangeable bases in the presence of

free calcium carbonate under field conditions. Since it is generally recognized that in ordinary soils the capacity for base exchange is seated in the colloidal complex which consists of clay and organic matter, W. attempts to ascertain the relative contributions of these two fractions to the base-exchange capacity of soils. He determined the total exchangeable bases, clay, total carbon, and carbon oxidizable by 4% hydrogen peroxide for a number of carbonate soils. Total exchangeable base content was determined in each case by decomposing the carbonate in a known weight of soil with acetic acid, estimating the carbon dioxide evolved, and further extracting with acetic acid to obtain a solution which contains not only the bases originally in combination with the CO_2 but also the exchangeable bases. The amount of the latter is then found by difference. Clay was determined by the so-called International Method, using 0.008 *N* sodium hydroxide for dispersion instead of aqueous ammonia. Total organic matter was determined by the method of Robinson, Maclean, and Williams (*ibid.*, **19**, 315 (1929)). The carbon content was also determined after digestion with 4% hydrogen peroxide. Assuming soils containing excess of carbonate under natural conditions to be base saturated, W. derived equations connecting exchange capacity with clay and (*a*) total, or (*b*) oxidizable carbon content. When the organic matter of these soils was assumed to have a constant base-exchange capacity, no correlation was found between the exchange capacity of their clay fractions and either their silica-alumina or silica-sesquioxide ratios. Carbonate soils whose exchangeable base content was appreciably less than the calculated values were found to contain either small amounts of calcium carbonate (less than 1%) or the bulk of it in coarse form. Soils which have been in contact with an efficient excess of finely divided calcium carbonate for a long period of time may be regarded as saturated, and it is suggested that the base-exchange content of such soil is the true measure of their base-exchange capacity. A comparison of the total exchangeable base content with the base-exchange capacity calculated from the clay and organic matter is suggested as a measure of the degree of saturation.

J.L.G.

Revised classification of soil types. E. B. DAVIES. *New Zealand Jour. Sci. & Tech.*, **14**, 255–56 (1933).—The 1904 scheme of classification of the U. S. Dept. of Agriculture is enlarged to cover 16 classes of sand, silt, loam, and clay. The type analyses of these classes are given in the paper. H.H.S.

Studies on the zeolites. III. Natrolite and metanatrolite. M. H. HEY AND F. A. BANNISTER. *Mineralog. Mag.*, **23** [139], 243–89 (1932).—Natrolite is shown by nine new analyses and new X-ray measurements to have a constant Si : Al ratio and a unit-cell formula of $Na_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$, in agreement with previous results. Na_2-Ca replacement may occur up to about 4, and Na-K replacement up to about 2 atoms per unit cell. Natural etch figures on natrolite from Benallt, Carnarvonshire (a new locality), show the *c*-axis to be polar. A detailed study of the optical properties of natrolite was made. Some observations were made on the effects of partial dehydration on the optical properties. The vapor pressure has been studied at various temperatures and degrees of hydration, and several peculiarities have been observed. The heat of hydration has been measured and shown to be in agreement with the vapor pressure work. Some experiments have been carried out on the base-exchange of natrolite. An X-ray study of natrolite and metanatrolite, together with the vapor pressure observations, suggests that natrolite is really monoclinic, with space group C_2^3, the symmetry-axis being parallel to the elongation (the usual *c*-axis), but there is marked pseudo-symmetry closely approaching that of the orthorhombic space group C_{2v}^{19}, of which C_2^3 is a subgroup. For Part I see *Ceram. Abs.*, **11** [5], 329 (1932). A.K.

Persistence of anisotropic structure in silica obtained from the action of acids on leucite. G. A. BLANC. *Atti accad. Lincei*, **16**, 3–6 (1932).—The crystal of hydrated SiO_2 obtained by the action of mineral acids on leucite retained, under certain conditions, the original crystalline form and structure of the complex $KAlSi_2O_6$. (*J.S.G.T.*)

English china clay: mining, mixing, and manufacturing. A. L. CURTIS. *Can. Chem. Met.*, **17** [6], 121–22 (1933); for abstract see *Ceram. Abs.*, **12** [6], 241 (1933).

E.J.V.

BOOKS AND BULLETINS

Structure of the Earth and the Movement of Its Surface: An Introduction to the Fundamentals of General Geology. (Der Bau der Erde und die Bewegung ihrer Oberfläche: eine Einführung in die grundfragen der allgemeinen Geologie.) W. VON SEIDLITZ. Verständliche Wissenschaft, Band 17. ix + 152 pp. Julius Springer, Berlin, 1932. 4.80 gold marks. Reviewed in *Nature*, **131** [3305], 318 (1933).—The origin of rocks is lucidly explained on sound principles. The main portion of the book

considers the movements to which the earth's crust has been subjected. The latter part contains a table of geological formations, a short bibliography, and a glossary. J.L.G.

Lead: Its Occurrence and Uses. Published by the Imperial Institute, London. 183 pp. 4s. Reviewed in *Metal Ind.* [London], **42** [21], 552 (1933).—The bulk of the book consists of a summary of information concerning the occurrence, geology, and mining of lead ores. An account of the concentration and metallurgy of lead ores, and the industrial uses of the metal, its alloys, and compounds are also given. M.V.K.

The Feldspars and Their Practical Determination. K. CHUDOBA. Reviewed in *Nature*, **131**, 384 (1933); see also *Ceram. Abs.*, **12** [1], 34 (1933). H.H.S.

Vermiculite. A. V. PETAR. Bur. Mines *Information Circ.*, No. 6720. 10 pp. Free. The term "vermiculite" is applied to a group of micaceous minerals that generally are alteration products of biotite, phlogopite, and other varieties of mica. Vermiculite is already an important ingredient of many insulating materials and interest in the material is growing. The report presents a brief description of properties, uses, domestic deposits, mining, and treatment of this mineral. A list of possible producers and consumers and a bibliography is attached. R.A.H.

Metal Resources of New Mexico and Their Economic Features. S. G. LASKY AND T. P. WOOTTON. Bur. Mines *Bull.*, No. 7, 178 pp. (1933).—The total metal production of N. M. from the advent of the Spaniards to 1930 is stated to have a value of 419 million dollars. About 80% of this amount is accounted for by mining operations from 1904 to 1930. Since the beginning of mining the value of the various metals produced has been as follows: copper $247,637,000, silver $51,645,000, gold $45,997,000, zinc $44,010,000, lead $18,140,000, iron ore $7,919,000, manganese and manganiferous ores $2,293,000, molybdenum $1,789,000, and tungsten ore $125,000. All available information of value to those interested in mining in N. M. has been assembled. All of the known mining districts are described briefly with attention to history, production, and geology. The uses of the metals and the marketing of the different ores are described. The section on the economic features of prospecting, mining, and milling contains important data on costs of construction and operation and should be of special value to those who are giving thought to acquiring or developing mining properties. Illustrated.

Introduction to symposium on industrial minerals in Canada. L. H. COLE. *Can. Mining Met. Bull.*, No. 255. 422 pp. Canada's position in respect to nonmetallic mineral production is outlined. G.M.H.

Geophysical Abstracts. No. 49. F. W. LEE. Bur. Mines *Periodical Service Rept.*, GA 49. 23 pp. A review is given of recent publications and patents relating to geophysical prospecting methods and instruments. For No. 48 see *Ceram. Abs.*, **12** [8], 311 (1933). R.A.H.

PATENT

Treatment of leucite, etc. T. J. I. CRAIG (Peter Spence & Sons, Ltd.). U. S. 1,914,404, June 20, 1933.

Chemistry and Physics

High-temperature preparation and the optical properties of sodium aluminate. K. KAMMERMEYER AND A. B. PECK. *Jour. Amer. Ceram. Soc.*, **16** [8], 363–66 (1933).

Colorimetric determination of aluminum with aurintricarboxylic acid. P. S. ROLLER. *Jour. Amer. Chem. Soc.*, **55** [6], 2437–38 (1933). F.G.H.

The Thomas recording gas calorimeter. R. S. JESSUP. Bur. Stand., *Jour. Research*, **10** [1], 99–121 (1933); R.P. 519.—The Thomas recording gas calorimeter is described. Calculations are made showing the effects on the reading of the calorimeter of change in temperature and barometric pressure. Results of comparisons of the Thomas calorimeter with the Junkers calorimeter on Washington City gas and on commercial propane are given. The agreement of the results obtained is well within the accuracy claimed for the Thomas calorimeter. Measurements of the lag of the Thomas calorimeter are described. It is stated that the Thomas calorimeter can be used to measure total heating values of gases well within 1% provided the calorimeter is given the necessary care and provided the heating value of the gas does not vary rapidly. R.A.H.

Infra-red arc spectra of manganese and rhenium. WILLIAM F. MEGGERS. Bur. Stand. *Jour. Research*, **10** [6], 757–69 (1933); R.P. 564.—New types of photographic plates sensitive to infra-red radiation are employed to explore the long-wave portions

of manganese and rhenium arc spectra from 7200 to 11,000 A. Many new lines have been recorded in each spectrum and these in turn have disclosed new spectral terms or atomic energy levels. R.A.H.

Influence of temperature on certain properties of zirconium oxide sols. F. J. ROBINSON AND G. H. AYRES. *Jour. Amer. Chem. Soc.*, **55** [6], 2288–94 (1933). F.G.H.

Equilibrium in systems of SiO_2, CaO, and Al_2O_3 with carbon. R. BRUNNER. *Z. Elektrochem.*, **38,** 55 (1932).—Mixtures of silica and carbon, alumina and carbon, and lime and carbon were electrically heated in a graphite tube in a vacuum furnace. Temperatures were optically measured through the open ends of the tube to 2000°. CO was introduced at various pressures and temperatures, and from the rates of reaction the conditions of zero reaction were calculated and equilibrium values of p and t plotted. In the system SiO_2 + C, a quintuple point was found, the phases being SiO_2, $(SiC)_2O$, SiC, C, and CO. A monovariance was found below the eutectic temperature for CaO and C mixtures. The equilibrium of the formation of aluminium metal and carbide was investigated. In all three systems sublimates formed by interaction of metal and carbon monoxide were detected. (*J.S.G.T.*)

Phase limits in systems of silica and alumina with carbon. E. BAUR. *Z. Elektrochem.*, **38,** 69 (1932).—A distinction was drawn between technical and laboratory conditions in the above systems in the experiments of R. Brunner (see preceding abstract). In the case of silicon and silicon carbide, these were formed at much lower temperatures in practice due to sudden heating and the effect of atmospheric pressure. (*J.S.G.T.*)

True softening point of silico-aluminous products. C. MEURICE. *Ind. chim. belge*, **3** [2], 112–17 (1932).—The curve of elongation *vs.* temperature is determined for a refractory in a certain apparatus. The curve of apparent deformation *vs.* temperature is also determined and by difference the true elongation curve on which the softening point is very sharply marked. (*C.A.*)

Viscosity of acid and basic open-hearth furnace slag in the molten state. TATUSO MATSUKAWA. *Suiyokwai-Shi*, **7,** 57 (1932).—The viscosities of molten slags from an acid and from a basic open-hearth furnace, containing 60 and 20% of SiO_2, respectively, were studied by the rotating cylinder method. At 1650 to 1700° the viscosity is the same as that of molten steel, but it increases with a slight decrease in temperature. The acid slag is much more viscous than the basic. Increase in the FeO content of the slag lowers the melting point and decreases the viscosity, while MnO raises the melting point and lowers the viscosity. The melting point of fayalite ($2FeO{\cdot}SiO_2$) is 1360°, of rhodonite ($MnO{\cdot}SiO_2$) 1255°, and of tephroite ($2MnO{\cdot}SiO_2$) about 1270°. (*T.C.S.E.*)

Shrinkage of mixes. L. A. SHMELEV. *Keram. i Steklo*, **9** [3], 18–19 (1933).—On the basis of practical observations relating to the shrinkage of clays and kaolins in connection with their swelling property, S. found the same dependence in mixes. Experimental data showed that the extent of swelling of the mix depends only on the swelling of clays and kaolins introduced in the composition of the mix. Materials not plastic have no influence on the rate of swelling. Owing to this property, the extent of swelling and of shrinking can be calculated with sufficient exactness when using a definite formula discussed by S. The practical importance of the formula is proved by experiments on various mixes. See also *Ceram. Abs.*, **12** [6], 245 (1933). M.V.K.

Fundamental laws of metallurgical reactions. W. OELSEN. *Z. tech. Physik*, **14** [6], 222–26 (1933).—Equilibria of metal and slag may be explained by the theoretical law of mass action. Deviations from this law will be caused by a nonideal behavior of molten metals and may be predicted from the solidification diagrams. Theoretical and practical results will agree for most systems unless metal and slag will disintegrate. See also article by Körber and Oelsen, *Ceram. Abs.*, **12** [6], 245 (1933). W.M.C.

Constitution of some simple cobalt and nickel compounds derived on the basis of their magnetic behavior. WILHELM KLEMM AND WILHELM SCHUTH. *Z. anorg. allgem. Chem.*, **210** [1], 33–56 (1933).—On the basis of the magnetic behavior of copper compounds it appears that in the oxide and bromide there are intermediate states between salt-like and metallic compounds at low temperatures; the compounds approach the metallic state at the lower temperatures and the salt-like state at the higher temperatures. Studies were made to determine if compounds of cobalt and nickel behaved similarly. Intermediate states of some of the compounds of these elements were found at low temperatures. L.T.B.

Preparatory separation of cerium from the remaining cerium ores. H. BJORN-ANDERSEN. *Z. anorg. allgem. Chem.*, **210** [1], 93–99 (1933).—A method is given for the

separation of cerium from other elements by precipitation as cerium chromate. There is also included a method for the determination of small amounts of R_2O_3 in cerium compounds. L.T.B.

Manufacture of titanium dioxide from sphene-apatites. V. E. TISHCHENKO, Y. M. PESIN, A. L. KOSTRAK, AND S. S. FREIDLIN. *Zhur. Prikladnoi Khim.*, **5**, 685–92 (1932).—Titanite is digested with 80% H_2SO_4 at 140 to 145° for 10 to 11 hr. The dry, powdered residue is extracted with H_2O at 97° for 7 hr., and the solution reduced with Fe and hydrolyzed, the product being washed and ignited at 500° for 3 hr. The yield of TiO_2 is 71%. (*B.C.A.*)

Test for lithium in the presence of other alkali ions; separation of lithium from magnesium, determination of lithium; separation of arsenites and arsenates. T. GASPAR. *Ann. chim. anal. chim. appl.*, **15**, 193–94 (1933); see following abstract. (*C.A.*)

Reagent for lithium ions; separation of lithium and magnesium; quantitative separation of arsenites and arsenates. T. GASPAR. *Anales soc. españ. fis. quím.*, **30**, 406 (1932).—A 5% alkali arsenite solution in MeOH or EtOH is the reagent. Of this, 3 to 5 cc. are added to 0.5 cc. of the solution to be tested and heated. If Li is present an abundant white or rose colored precipitate forms quantitatively. The separation of Mg from Li by the aid of arsenites is similar. Arsenites are separated from arsenates by the aid of LiCl in NH_4OH-EtOH solution and filtered, and in the filtrate the arsenites are precipitated by $MgCl_2$. (*C.A.*)

Rapid rational analysis for fired clay by the 8-hydroxyquinoline-acetate method. TAKEO AO. *Jour. Soc. Chem. Ind.* [Japan], **35** [12], 567*B* (1932).—The dissolving of fired feldspar and Kato-kaolin in 10% hydrochloric acid solution was studied. It was found that feldspar is almost insoluble in the acid, while in Kato-kaolin the quantity of alumina dissolved increases with increasing temperature. At 800°C almost all Al_2O_3 is extracted in fired Kato-kaolin. A great number of determinations of the soluble Al_2O_3 obtained was made volumetrically by means of the 8-hydroxyquinoline-acetate method and also gravimetrically; the difference between the two methods is never greater than 0.7%. The 8-hydroxyquinoline-acetate method is very rapid. M.V.K.

Precipitation and titration of magnesium oxyquinolate in the presence of calcium oxalate and its application in the analysis of Portland cement and similar silicates. JOHN C. REDMOND. Bur. Stand. *Jour. Research*, **10** [6], 823–26 (1933); R.P. 569.—Data are presented showing that magnesium oxyquinolate can be precipitated and titrated in the presence of calcium oxalate. A rapid method for the determination of magnesium in Portland cements is described. R.A.H.

Data. XVII. T. W. GARVE. *Clay-Worker*, **99** [6], 210–11 (1933).—Definitions, manufacturing details, physical characteristics, and strengths are given for sewer pipe, architectural terra cotta, and floor and wall tile, with the various classes under each of these headings enumerated. For Part XVI see *Ceram. Abs.*, **12** [8], 298 (1933). E.J.V.

Behavior of ceramic materials in tension, compression, and fatigue. A. THUN. *Z. Ver. deut. Ing.*, **77** [14], 365 (1933).—A résumé is given of Prof. Esau's work in which he has shown that ceramic materials fail under fatigue tests. The behavior in some cases is similar to that shown by metals under similar testing conditions. L.T.B.

Dispersion and deflocculation of certain soils. E. B. DAVIES. *New Zealand Jour. Sci. & Tech.*, **14**, 228–32 (1933).—Certain soils from Taranaki Province could not be mechanically analyzed by the usual methods. Motor dispersion and the omission of alkaline deflocculents removed the difficulties. H.H.S.

Method of carrying out "spot" tests. J. WINKELMANN. *Mikrochemie*, **12**, 119–28 (1932); *Analyst*, **58**, 116 (1933).—Gelatin or glycerin jelly affords a medium which allows of permanent preparations for mounting. H.H.S.

BOOKS

Prescott and Johnson's Qualitative Chemical Analysis. R. K. MCALPINE AND B. A. SOULE. D. Van Nostrand, New York, N. Y. 696 pp. Price $4.50. *Can. Chem. Met.*, **17** [5], 55 (1933). E.J.V.

Elementary Quantitative Analysis. Theory and Practice. H. H. WILLARD AND N. H. FURMAN. D. Van Nostrand Company, Inc., New York, 1933. *Jour. Amer. Chem. Soc.*, **55** [7], 3064 (1933). F.G.H.

Annual Survey of American Chemistry. Vol. VII, 1932. Edited by C. J. West. Published for National Research Council by the Chemical Catalog Company, Inc., New

York. 346 pp. Price $4.00. *Jour. Amer. Chem. Soc.*, **55** [7], 3064 (1933); for Vol. VI see *Ceram. Abs.*, **11** [9], 510 (1932). F.G.H.

Fundamentals of Physical Chemistry. E. C. H. DAVIES. Blackiston's Sons, Philadelphia, 1932. 377 pp. Price $2.75. *Jour. Inst. Metals*, **53** [3], 173 (1933). F.G.H.

Modern Physics. G. E. M. JAUNCEY. D. Van Nostrand Co., New York, 1932. 568 pp. Price $4.00. *Mech. Eng.*, **55** [2], 143 (1933). F.G.H.

Hydrogen-Ion Concentration. F. L. LA MOTTE. Bailliere, Tindall, and Cox, London, 1933. Price 21s 6d net. *Jour. Inst. Metals*, **53** [3], 175 (1933). F.G.H.

PATENTS

Manufacture of pigments. F. G. A. STUTZ AND H. A. DEPEW (New Jersey Zinc Co.). U. S. 1,914,539, June 20, 1933.

Zirconium, silicon, and alkali metal solutions, and methods of making. C. J. KINZIE (Titanium Alloy Mfg. Co.). U. S. 1,916,226, July 4, 1933. (1) A method of converting zirconium silicate or zircon into an acid zirconium solution containing silicon and an alkali metal comprises heating the zirconium silicate with the alkali to substantially complete decomposition, treating the roasted product with acid in amount less than theoretically required to form normal salts with the zirconium and alkali to make a solution of silicon and soluble zirconium compounds, and separating the clear acid liquor containing zirconium, silicon, and the alkali metal in solution. (2) As a new article, a nitrate zirconium solution has silicon and alkali metal salts in solution and no free acid.

Method of precipitating titanium compounds. L. W. RYAN (Titanium Pigment Co., Inc.). U. S. 1,916,236, July 4, 1933. In the precipitation of titanium compounds by hydrolysis from a mineral acid solution containing titanium, the steps consist in dissolving an organic acid in the solution and thereafter adding the resultant solution to hot water.

Process for the preparation of alkaline earth aluminates. JOSEF STÖHR (Lonza-Werke Elektrochemische Fabriken G.m.b.H.). U. S. 1,916,697, July 4, 1933. (1) The process of preparing calcium aluminate comprises preparing a melt consisting of calcium carbide and calcium oxide at an excessively high temperature, introducing into the melt an aluminous material, drawing off the metal alloy formed by reduction of the impurities of the aluminous compound, subsequently drawing off the molten aluminate, and disintegrating it. (2) The process of preparing alkaline earth aluminates comprises thoroughly mixing about 300 parts of calcined lime with about 125 parts of anthracite, melting the mixture in an electric furnace to establish a molten bath at an excessively high temperature and to cause a reaction producing calcium carbide, introducing into the molten bath at an excessively high temperature about 900 parts of dried bauxite, continuing the application of heat to maintain the bath in a molten condition and to cause a reaction producing calcium aluminate and an alloy containing iron, silicon, and titanium, permitting the molten bath to stratify whereby the alloy containing iron, silicon, titanium, and impurities sinks to the bottom thereof and relatively pure calcium aluminate floats to the top thereof, and tapping the alloy from the bath whereby relatively pure calcium aluminate is produced.

Manufacture of boric acid. ANDREW KELLY (Borax Consolidated, Ltd.). U. S. 1,918,110, July 11, 1933.

Preparation of titanium compounds. H. SPENCE, W. B. LLEWELLYN, AND P. SPENCE & SONS, LTD. Brit. 393,264, June 14, 1933.

Removing iron from quartz sand, clay, bauxite, etc. SOCIÉTÉ DES PRODUITS CHIMIQUES "ALTERRA" A.-G. Ger. 572,195, May 3, 1930. The material is treated at atmospheric or raised temperature with dilute H_2SO_4 containing at least 4% of $FeSO_4$. If carbonates of Ca and Mg are present, the material should be pretreated with H_2SO_3 at atmospheric or moderately raised temperature and pressure, the pretreatment being stopped as soon as the evolution of CO_2 ceases. Examples and numerous details are given. (*C.A.*)

Removing iron from bauxite, kaolin, heavy spar, etc. FREDERIC VAN TAACK-TRAKRANEN AND HANS WOLF (I. G. Farbenind. A.-G.) Ger. 573,283, May 27, 1930. The material is treated with a solution of HCl in an organic solvent such as ether or acetone. (*C.A.*)

General

The Bulletin of the American Ceramic Society. EDITORIAL. *Bull. Amer. Ceram. Soc.*, **12** [7], 213–14 (1933).

Position taken by Patent Office that siliceous compositions fired to 1500°F are not ceramic. ANON. *Bull. Amer. Ceram. Soc.*, **12** [7], 220 (1933).

Place of the university in industrial research. B. M. WOODS. *Mech. Eng.*, **55** [3], 167–68 (1933). F.G.H.

Educational preparation for creative technical engineering leadership. R. E. DOHERTY. *Mech. Eng.*, **55** [2], 90–94 (1933).—The acquisition of knowledge and of proficiency in manipulative techniques is only one-half of our educational objective in engineering. The other half is the art of utilization of knowledge. Methods of attaining these objectives in the technical training offered by our colleges are discussed. F.G.H.

Basic structure of the ceramic industries. A. V. BLEININGER. *Bull. Amer. Ceram. Soc.*, **12** [7], 214–20 (1933).

Advances in knowledge of ceramic materials. W. STEGER. *Z. Ver. deut. Ing.*, **77** [4], 81–87 (1933).—The properties of ceramic materials, present demands and requirements, improvement in quality, and the advances in technical knowledge are discussed. The materials include hollow ware for walls and roofs, insulating materials, refractory materials, alumina-free materials, molten materials, silicon carbide blocks, chrome and zircon ores, magnesite block with low-temperature coefficient, porous ware, porcelains for chemical and electrical purposes, porcelains for pyrometers, materials for special purposes, corundum, silicon carbide for the electrical industry, and others. Testing data for many of these ceramic materials are summarized in orderly tables; the data include tensile, compressive, and bending strengths, porosity, specific weight, modulus of elasticity, softening points, and heat conductance. L.T.B.

Time analysis and motion study. FRANK CERMAK. *Bull. Amer. Ceram. Soc.*, **12** [7], 224–26 (1933).

Time-study application in the ceramic industry. C. K. ANDREW. *Bull. Amer. Ceram. Soc.*, **12** [7], 221–23 (1933); see also *Ceram. Abs.*, **11** [9], 509 (1932).

Obtaining sodium silicate from sand and sulfate from Karabugaz. S. YA. RAP. *Keram. i Steklo*, **9** [3], 24–25 (1933).—R. describes in detail attempts made to manufacture sodium silicate from sand (98.64% SiO_2) and sulfate (95% Na_2SO_4) from Karabugaz. The results were as follows: (1) a sodium silicate of the composition 50% Na_2O and 50% SiO_2 was not obtained because of the presence of different admixtures in the sulfate which remained in the silicate. (2) The average temperature of fusing of the silicate is about 1350 to 1370°. (3) The average length of fusing is from 5 to 6 hr. (4) Grog brick were found to be the most stable. (5) With the increase of the number of sodium silicate fusions, the refractories become considerably affected and their component parts such as SiO_2, Al_2O_3, and others combine with the silicate. M.V.K.

Silicosis. ANON. *Bull. Amer. Ceram. Soc.*, **12** [7], 233–35 (1933).

Dust in industry. A. E. RUSSELL. *Mech. Eng.*, **55** [3], 163–66 (1933).—The economic and hygienic aspects of silicosis are discussed under the following headings: (1) chemistry and petrography of dust, (2) condition of worker at the beginning of exposure, (3) length of exposure, concentration, and size of particles, (4) effects produced, and (5) course of silicosis among workers no longer exposed to silica dust. F.G.H.

Dust in industry. F. WILLSON. *Mech. Eng.*, **55** [2], 80–82 (1933).—Shop methods and equipment effective in controlling dust hazards are described. Various dust-exhausting systems are compared. The use of respirators is discussed. The necessity for close coöperation between the management and the workmen is emphasized. Illustrated. F.G.H.

Dedication of new ceramic building at New York State College of Ceramics. ANON. *Bull. Amer. Ceram. Soc.*, **12** [7], 235–37 (1933).

Haida State Technical School and the local glass industry. J. B. *Glas und Keram. Ind.*, **23** [11*s*], 11 (1932).—This school, established in 1870 for the education of the local glassworkers, is provided with the most up-to-date equipment. The system of instruction enables the students to become familiar with modern methods of production, while frequent visits to other factories and to museums help to extend their knowledge of the glass art, past and present. Exhibitions of school work are held every two years in order to show the public the standard of excellence of the students. Special instruction is given in chemistry and in the composition and coloring of glass so that the local factories still operating on an empirical basis are deriving considerable benefit. (*J.S.G.T.*)

Report on the first school year of the Silesian Glass Technology School at Bunzlau,

Silesia. BERDEL. *Glashütte*, **62**, 335–36 (1932).—Eight pupils attended the summer term and 15 the winter. The school is well equipped, several gifts of apparatus and equipment having been added during the year. A special feature was the attendance of pupils from the Ceramic School for occasional lectures on glass technology, while the glass technology pupils were likewise reciprocally welcomed to the Ceramic School. A close coöperation is maintained with the local glass industries in the matter of carrying out tests on their productions. The syllabus includes the usual chemical, physical, engineering, and technical subjects. For the 1932 summer term, 26 pupils were enrolled. (*J.S.G.T.*)

Gablonz Glass Institute in 1931. ANON. *Glas und Keram. Ind.*, **23** [11*s*], 10 (1932).—At the annual general meeting of the Institute reports were submitted dealing with the difficulties encountered in an attempt to suppress industrial espionage and piracy during the year. Trade depression has been the means of diverting a considerable amount of work from the industrial areas to the rural districts. Committees were formed to investigate the economics of this situation. A bureau was set up to give information regarding financially unstable firms. A reform of the law relating to patent rights of designs was desirable. The contribution toward sick benefit insurance was increased, but a discussion of the insurance of home workers led to no agreement. (*J.S.G.T.*)

German State Technical School for the glass industry at Stein-Schönau, Bohemia. ANON. *Glas und Keram. Ind.*, **23** [11*s*], 11 (1932).—This school, established 76 years ago, with its own library and museum, was organized on practical lines, equipped with the most modern technical plant and machinery, and with a staff of qualified instructors and experts. It is divided into the following departments: (1) the technical school where all phases of the art of glassmaking are taught, (2) school for apprentices, and (3) school for special instruction. After the completion of their studies, the pupils are absorbed into the special branches of the industry for which they are particularly suited. The school, since its inception, has proved of great benefit to the glass industry generally throughout the whole of Northern Bohemia and has become an important life center of the industry. (*J.S.G.T.*)

Touring A Century of Progress for the ceramist. ANON. *Ceram. Ind.*, **21** [1], 34–44 (1933).—This article, with diagrams and illustrations, points out the features of A Century of Progress which are of ceramic interest. W.W.M.

Three days for brickmakers, 1933. ANON. *Tonind.-Ztg.*, **57** [28], 335–36; [30], 357–59; [31–32], 370–71 (1933).—During the second day of the meeting, the following papers were read and discussed: (1) Brick and tile for masonry and ceilings, by Siedler; (2) Problems facing the roofing tile manufacturers, by Hofherr (*Ceram. Abs.*, **12** [8], 316 (1933)); (3) Hard-fired brick for road construction, by A. Hielscher (*ibid.*, **12** [8], 298 (1933)); (4) Contributions of the ceramic industry toward small settlements and amelioration projects, by W. Gross; (5) Coöperation of the clay, lime, and mortar industries, by K. A. Goslich; (6) Present condition of the German brick industry and brick constructions, by Mauss; (7) Small comfortable brick houses, by Lee (*ibid.*, **12** [6], 225 (1933)); and (8) Installation and management of a terra cotta plant, by Kabus. W.M.C.

BOOKS AND BULLETIN

Recent Trends in American Housing. EDITH E. WOOD. Macmillan Co., New York, N. Y. Price $3.00. *Brick Clay Rec.*, **82** [6], 203–204 (1933).—W. takes up modern trends in American housing, having first made a careful summary of housing evils and their remedies. The book is filled with startling statistics, comparisons, and statements which should shake us out of our lethargy about housing conditions. E.J.V.

A History of the Home. ALBERT FARWELL BEMIS AND JOHN BURCHARD, 2ND. Massachusetts Institute of Technology, Technology Press, Cambridge, Mass. Price $4.00. *Brick Clay Rec.*, **82** [6], 203 (1933).—This is the first of three volumes to be published on "The Evolving House." The beginning of ceramics is noted as the first cultural advance of the neolithic man. E.J.V.

Square-set system of mining. E. D. GARDNER AND W. O. VANDERBURG. Bur. Mines *Information Circ.*, No. 6691. 73 pp. The report discusses history, factors affecting use, construction, development work, stoping practices with square-set system, and cost of mining by square-set methods. R.A.H.